PHYSICAL REVIEW B VOLUME 27, NUMBER 6 15 MARCH 1983

Temperature and pressure dependences of the dielectric constants of semiconductors

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(Received 7 September 1982)

The effects of temperature and hydrostatic pressure on the static dielectric constant (ϵ) were investigated for a group of crystalline semiconductors chosen to be representative of III-V compounds (GaAs and GaP), II-VI compounds (ZnS and CdS), and group-IV (Si) materials. When combined with earlier results on the temperature and pressure dependences of the high-frequency optical (i.e., electronic) dielectric constants (ϵ_∞), the present results allow, for the compound semiconductors, determination of the lattice contribution to these effects. The results are discussed from both the microscopic and macroscopic points of view. For all the crystals studied, the pressure effects are dominated by the change in polarizability with volume, and the temperature effects by anharmonicities. The pressure dependences of the lattice contributions to the dielectric constants (ϵ_{11} and ϵ_{33}) of hexagonal CdS are anomalous in that they increase with pressure. This behavior is most likely due to coupling between the appropriate TO modes and the TA modes which are known to soften on approaching the pressure-induced phase transition in this crystal. The transverse dynamic effective charge was calculated for the compounds, and its pressure dependence was determined for GaAs and GaP. The results and their implications are discussed.

I. INTRODUCTION

The dielectric constants of a semiconductor are among its most important properties. Their magnitudes and temperature dependences are important for both fundamental and applied considerations. These properties enter in an important way into the physics underlying the optical, transport, and lattice-dynamical properties of semiconductors, and they are also important in considerations of defect and impurity states. It is thus necessary to understand the dielectric properties and their temperature dependences in terms of the various mechanisms of dielectric polarization. Toward this end we have investigated the effects of temperature and hydrostatic pressure on the low-frequency dielectric constants of several crystals representative of III-V compounds (GaAs and GaP), II-VI compounds (ZnS and CdS), and group-IV (Si) semiconductors. Combined with earlier results on the temperature and pressure dependences of the high-frequency (or optical) dielectric constants, the present results allow us to evaluate, for the compound semiconductors, the lattice contribution to these effects.

There appear to be no earlier pressure studies on the static dielectric constants of GaAs, GaP, ZnS, and CdS, but there are some results on Si.[1,2] Some data on the temperature dependences of the dielectric constants at atmospheric pressure have been reported. These include results on GaAs in the temperature range 100—300 K,[3,4] on CdS in the range 4—300 K,[5] on Si in the range 4—300 K,[1,6] and values of the dielectric constant at a few temperatures for GaP (Refs. 7 and 8) and ZnS.[9] In the next section we discuss briefly the experimental details, and the following two sections present the results and their interpretation.

II. EXPERIMENTAL DETAILS

High-resistivity single crystals of GaAs, GaP, cubic ZnS, CdS, and Si were used in this study. GaAs, GaP, and ZnS have the cubic zinc-blende structure, CdS has the hexagonal wurtzite structure, and Si has the cubic diamond structure. Samples were cut in the form of thin plates about 0.5 mm thick by about 0.5 cm^2 in area, and, for the cubic crystal, were oriented with the thickness direction perpendicular to the [100] face. For CdS both *a*-axis— and *c*-axis—oriented samples were used. Gold, chrome-gold, or aluminum electrodes were vapor deposited on the large sample faces. Only samples which had bias-independent noninjecting contacts in the temperature ranges of interest were selected for study.

The static dielectric constants were determined from low-frequency (10—100 kHz) capacitance measurements with the use of high-accuracy ($>$ 0.1%) three-terminal capacitance bridges and shielded leads and sample holders. The details were similar to those in earlier studies.[10] In some temperature ranges the capacitance and dielectric loss tanδ were strongly frequency dependent. All the data used for the analysis in Secs. III and IV were taken under conditions where the capacitance was frequency independent and $\tan\delta \lesssim 0.01$.

Temperature and pressure measurements were performed in a maraging steel pressure cell mounted inside a conventional low-temperature Dewar.[10] This cell is capable of containing pressures up to ~ 1.2 GPa ($=12$ kbar). Helium gas was the pressure fluid and the pressure was measured to better than 1% by a calibrated manganin gauge. Temperature changes were measured to better than 0.1 K using Cu-Constantan and Cu-AuFe thermocouples.

The real part of the dielectric constant (ϵ) and its change with temperature and pressure were calculated from the measured capacitance by correcting for changes in sample dimensions due to thermal expansion and compression as described earlier.[10] In the case of CdS account is made of the fact that this crystal is not cubic. Values of the needed axial and volume compressibilities were taken from the literature or were evaluated from available elastic constants, and the thermal expansivities were taken from the literature. These values, which will also be needed for the interpretation of the results, are summarized in Table I. Owing to uncertainties in the dimensions of samples and various small corrections, the absolute accuracies of the dielectric constants to be reported in Secs. II and III are limited to only $\sim \pm 3\%$. Relative changes, including temperature and pressure derivatives, should, however, be more accurate.

III. EXPERIMENTAL RESULTS

A. Gallium arsenide

Figure 1 shows the temperature dependences of the real part of the static dielectric constant ϵ, and of the dielectric loss $\tan\delta$, at atmospheric pressure. The sample was a Cr-doped high-resistivity single crystal. Below ~ 150 K there is no frequency dependence to these quantities between 1 and 100 kHz, but strong frequency dependence is observed at higher temperatures. This is associated with dipolar contributions which become activated at higher temperatures. The $\epsilon(T)$ response becomes frequency independent at 100 kHz up to ~ 300 K and this represents the true $\epsilon(T)$ of the crystal. Between 300 and 350 K there is still a small frequency dependence, and this is represented in Fig. 1 by the deviation of the 100-kHz data (circles) from the dashed curve.

The deviations of $\epsilon(T)$ from the true response at the higher temperatures are associated with large increases in $\tan\delta(T)$, i.e., in sample conductivity (since $\tan\delta = 4\pi\sigma/\epsilon\omega$, where σ is the conductivity and ω is the measuring frequency[10]). This is depicted in the lower portion of Fig. 1.

Earlier measurements of ϵ of GaAs have yielded widely different values ranging from 9.8 to 13.3 at room temperature.[11] Our value of $13.19 \pm 3\%$ at 300 K is in good agreement with the results of Strzalkowski *et al.*[3] and of Champlin and Glover.[4]

The temperature dependence of ϵ of GaAs at atmospheric pressure has been reported earlier by Champlin and Glover[4] and by Strzalkowski *et al.*[3] for $100 < T < 300$ K. Both groups report a nearly linear $\epsilon(T)$ response over this limited temperature range, but the $\epsilon(T)$ slopes are markedly different. Our $\epsilon(T)$ results in Fig. 1 extend over a significantly broader temperature range than these earlier studies, and clearly show that the response is nonlinear. We

TABLE I. Room-temperature values of the axial compressibilities $\kappa_a \equiv -(\partial \ln a/\partial P)_T$, axial thermal expansivities $\beta_a \equiv (\partial \ln a/\partial T)_P$, and the long-wavelength ($\vec{q}=0$) transverse- and longitudinal-optic—mode frequencies for the various crystals of interest in the present work.

	κ_a[a] (10^{-3} GPa^{-1})	β_a[b] (10^{-6} K^{-1})	$\omega_{\rm LO}$ (cm^{-1})	$\omega_{\rm TO}$ (cm^{-1})
GaAs	4.46	5.7	292[e]	269[e]
GaP	3.76	5.3	401[f]	366[f]
ZnS	4.26	6.7	350[f]	274[f]
CdS (*a* axis)	5.40[c]	5.0[d]	307[g]	243[g]
CdS (*c* axis)	5.80[c]	2.5[d]	304[g]	235[g]
Ge	4.43	5.7		
Si	3.40	2.5		
C	0.73	1.1		

[a] Calculated from the elastic constants listed in R. M. Martin, Phys. Rev. B 1, 4005 (1970).

[b] Values taken from tabulations in Refs. 14 and 15.

[c] E. Gutsche, Naturwissenschaften 45, 486 (1958).

[d] Values taken from R. R. Reeber, and B. A. Kulp, Trans. Metall. Soc. AIME 233, 698 (1965).

[e] Values from Ref. 25.

[f] Values taken from tabulation in Ref. 12.

[g] Values from R. J. Briggs and A. K. Ramdas, Phys. Rev. B 12, 5518 (1976).

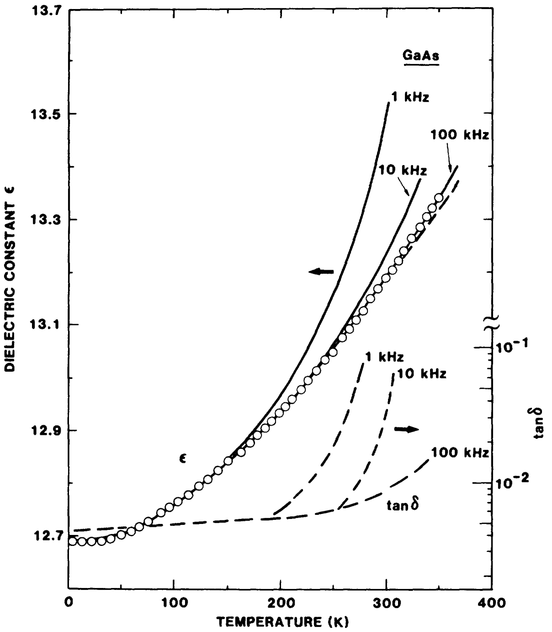

FIG. 1. Temperature dependences of the static dielectric constant (ϵ) and dielectric loss (tanδ) of GaAs at different frequencies at atmospheric pressure. For clarity, the actual data points at only one frequency (100 kHz) are shown. Data have been corrected for dimensional changes due to thermal expansion.

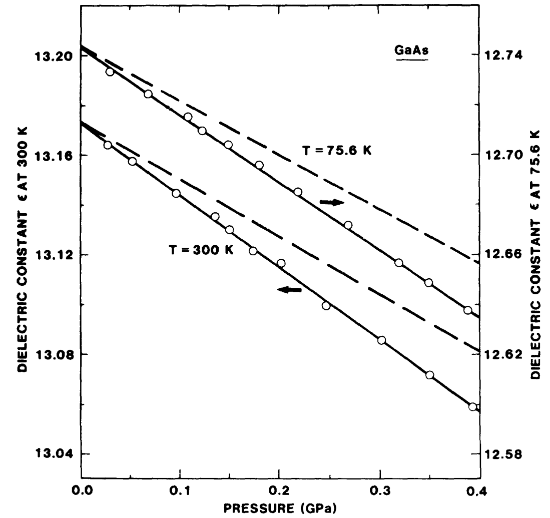

FIG. 2. Hydrostatic pressure dependence of the static dielectric constant of GaP at two temperatures. Dashed lines represent the response corrected for the changes in the dimensions of the sample due to the finite compressibility of GaAs.

note that our results yield $d\epsilon/dT \rightarrow 0$ as $T \rightarrow 0$ K as is expected on thermodynamic grounds. Strzalkowski *et al.*[3] extrapolated their high-temperature data linearly to 0 K to obtain a 0-K value of $\epsilon = 12.35$. This linear extrapolation is incorrect and leads to a too small a value of ϵ.

Figure 2 shows the pressure dependences of ϵ at 300 and 75.6 K for the same GaAs sample as in Fig. 1. The circles reflect the actual measured changes in sample capacitance, whereas the dashed lines represent the response corrected for the changes in the dimensions of the sample due to the finite compressibility of the crystal. Note that the corrections are substantial. (By comparison the corrections for thermal expansion in Fig. 1 are relatively much smaller.) tanδ exhibits a small monotonic decrease with increasing pressure. The $\epsilon(P)$ responses in Fig. 2 are seen to be linear over the pressure range covered. The logarithmic pressure derivatives at the two temperatures are listed in Table II where they are compared with similar results on some of the

TABLE II. Values of the real part (ϵ) of the static dielectric constant and its logarithmic temperature and pressure derivatives for various compound semiconductors deduced from the present results.

	T (κ)	ϵ	$(\partial \ln\epsilon/\partial T)_P$ (10^{-5} K^{-1})	$(\partial \ln\epsilon/\partial P)_T$ (10^{-3} GPa^{-1})
GaAS	300	13.18	20.4±0.3	−17.3±0.3
	75.6	12.74	9.4±0.4	−16.7±0.3
GaP	300	11.11	11.4±0.3	−10.8±0.2
	75.7	10.86	5.4±0.2	−9.7±0.2
ZnS	300	8.3	11.0[a]	−10.8±0.6[b]
	75.6	8.1		−10.4±0.5
CdS (*c* axis)	300	10.21	22.0±0.5	+13.2±0.5
CdS (*a* axis)	300	8.99	18.7±0.5	+3.9±0.5

[a] Estimated from Ref. 9. This value may be relatively inaccurate, but this is not expected to affect the qualitative conclusions drawn in Sec. IV.

[b] See discussion in Sec. III.

other crystals. The observed decrease in the $\epsilon(P)$ slope with decreasing temperature is characteristic of all of the materials studied. There appear to be no earlier data to compare the present $\epsilon(P)$ results with.

In view of the fact that ϵ does not change appreciably with T between 75 and 4 K (Fig. 1), and the result that the pressure dependence of ϵ is weakly temperature dependent, we expect the pressure dependence of ϵ at 4 K to be approximately the same as that at 75.6 K given in Fig. 2 and Table II.

B. Gallium phosphide

The temperature dependences of ϵ and $\tan\delta$ of GaP at atmospheric pressure are shown in Fig. 3. The results are qualitatively similar to those for GaAs; however, the larger band gap of GaP and higher resistivity ($>10^9$ Ω cm at 300 K) of the sample used made it possible to extend these measurements to higher temperatures than was possible with GaAs. The frequency-independent range of the data extends to $\sim$400 K, and even at 500 K the 100-kHz data (circles) deviate only slightly from the true response (dashed line). The dielectric loss $\tan\delta$ of this sample is much lower than that for the GaAs sample. The origin of the unusually high resistivity of the sample is not known but is believed to be chromium and/or oxygen doping. Both substances introduce deep centers in GaP.

At 295 K, $\epsilon = 11.2 \pm 3\%$. This is to be compared with the value of 11.1 deduced from optical data by Barker.[7] The temperature dependence of ϵ apparently has not been reported explicitly; however, a value of 10.75 ± 0.1 at 1.4 K has been reported by Patrick and Dean.[8] Our results below 10 K agree with this value within experimental uncertainties.

The pressure dependences of ϵ of GaP at 298.4 and 75.7 K are shown in the inset of Fig. 3, where the data have been corrected for dimensional changes. These results are qualitatively similar to those for GaAs in Fig. 2. The logarithmic pressure derivatives are given in Table II. The decrease in this derivative with decreasing T is similar to that observed for GaAs.

C. Cadmium sulfide

Cadmium sulfide has the hexagonal wurtzite structure and thus two dielectric constants, the a-axis (or ϵ_{11}) and the c-axis (or ϵ_{33}) constants. Figure 4 shows the temperature dependences of both ϵ_{11} and ϵ_{33}. These data were obtained in the range 76–320 K from measurements at 100 kHz. Under these conditions $\tan\delta$ was always less than 0.001. At 100 kHz the measured response reflected the true response of the crystal, whereas at lower frequencies there were deviations (similar to those in Figs. 1 and 3) at temperatures above 260 K. The results in Fig. 4 are in good agreement with the recent results of Kobiakov determined by a resonance technique.[5] The extension of our data in Fig. 4 from 76 to 4 K (represented by the dashed lines) was guided by Kobiakov's results.

The pressure dependences of ϵ_{11} and ϵ_{33} at 300 K are shown in the inset of Fig. 4, where the data have been corrected for the known axial compressibilities. Before this correction the measured $\epsilon_{11}(P)$ response (i.e., the capacitance) shows a slight linear decrease with pressure whereas $\epsilon_{33}(P)$ shows a linear increase. The responses in Fig. 4 are clearly anomalous when compared with the other semiconductors studied in that both ϵ's increase (instead of decrease) with pressure. We shall analyze and discuss these results in Sec. IV.

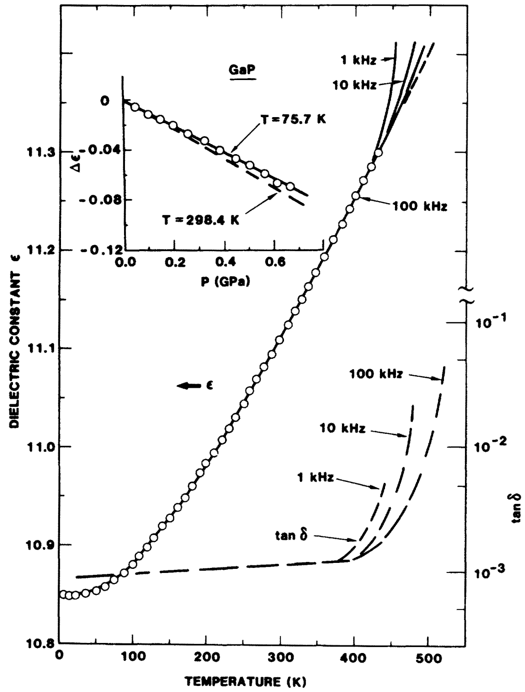

FIG. 3. Temperature dependences of the static dielectric constant (ϵ) and dielectric loss ($\tan\delta$) of GaP at different frequencies at atmospheric pressure. For clarity, the actual $\epsilon(T)$ at only one frequency (100 kHz) are shown. Inset shows the decrease of ϵ with hydrostatic pressure at two temperatures. For clarity, only the 75.7-K data are shown.

D. Zinc sulfide

The small sample of this material that was used was quite lossy at room temperature ($\tan\delta \approx 0.15$ at

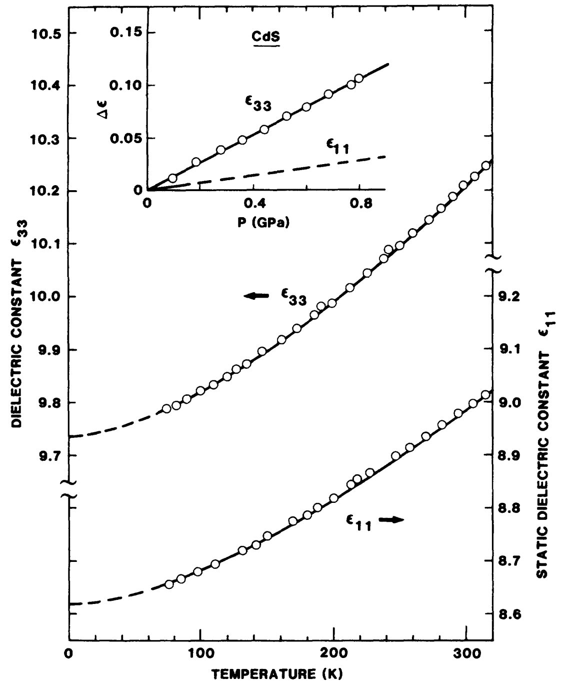

FIG. 4. Temperature dependences of the *a*-axis (ϵ_{11}) and *c*-axis (ϵ_{33}) static dielectric constants of CdS at atmospheric pressure. Data were taken at 100 kHz. Inset shows the anomalous hydrostatic pressure dependences of ϵ_{11} and ϵ_{33} at 300 K. Results have been corrected for dimensional changes due to the finite compressibility of CdS.

100 kHz) and the $\epsilon(T)$ response was strongly frequency dependent. At 75.7 K, tanδ had decreased to 0.07. The $\epsilon(T)$ response between 75.7 and 300 K was nearly linear, but because of the high dielectric loss the absolute accuracy of the data is uncertain especially at the high temperatures. For this reason we shall rely on results in the literature for the 300-K temperature derivative of ϵ used in the analysis in Sec. IV.

The pressure dependences of ϵ at 300 and 75.6 K are shown in Fig. 5, where the data have been corrected for the compressibility of the sample. tanδ decreased monotonically with increasing pressure at both temperatures. The logarithmic pressure derivates of ϵ are given in Table II. At 75.6 K the dielectric loss was sufficiently low and the $\epsilon(P)$ in Fig. 5 should represent the true response of the sample. By analogy with GaAs, GaP, and other materials, we expect the 300-K slope of the $\epsilon(P)$ response to be slightly larger than that at 75.6 K. This is reflected by the data in Fig. 5; however, the 300-K slope,

$$\frac{\partial \ln \epsilon}{\partial P} = -12.0 \times 10^{-3} ,$$

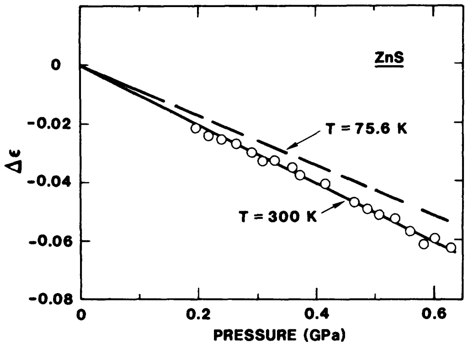

FIG. 5. Hydrostatic pressure dependence of the static dielectric constant of cubic ZnS at two temperatures. At atmospheric pressure $\epsilon = 8.30$ at 300 K and 8.10 at 75.6 K.

in units of GPa^{-1}, may be somewhat too high because of the high loss (but it should represent the upper limit of $\partial \ln \epsilon / \partial P$ at 300 K). Based on the 75.6-K slope for ZnS, and by analogy with the GaAs and GaP results, we shall use

$$\frac{\partial \ln \epsilon}{\partial P} = -(10.8 \pm 0.6) \times 10^{-3}$$

(in GPa^{-1}) instead of the measured -12.0×10^{-3} GPa^{-1} in the analysis of the data in Sec. IV.

E. Silicon

Several high-resistivity ($> 3 \times 10^3$ Ω cm) Si samples were examined, and in all cases it was possible to obtain the true ϵ response only below ~30 K. Above this temperature the activation of residual shallow impurities interfered. Below 30 K the temperature dependence of ϵ was negligibly small and the pressure dependence was significantly smaller than that for the other crystals studied. We observed a small decrease in ϵ with pressure comparable to that reported earlier,[1] but the scatter in the data was such as to render the results relatively inaccurate.

Since Si is a homopolar semiconductor with a center of inversion symmetry between the atoms, its static dielectric constant (ϵ) is simply the square of the long-wavelength refractive index (n). The temperature and pressure dependences of n of Si have been measured using optical (interferometric) techniques.[1,2] These techniques yield higher accuracy than is possible by the capacitance method. For this reason we have made use of the $n(T,P)$ data[1,2] to evaluate the temperature and pressure derivatives of ϵ listed in Table III. These latter results, along with the similar results on germanium (Ge) and diamond (C) also listed, will be used for comparative purposes in Sec. IV. For both Si and Ge we have selected for

TABLE III. Room-temperature (300-K) values of the optical dielectric constant ϵ_∞ and its logarithmic temperature and pressure derivatives for the various semiconductors of present interest. Data are taken from the literature where the results were expressed in terms of the index of refraction n. Note that $\epsilon_\infty = n^2$.

	ϵ_∞	$(\partial \ln\epsilon_\infty/\partial T)_P$[a] ($10^{-5}$ K^{-1})	$(\partial \ln\epsilon_\infty/\partial P)_T$ (10^{-3} GPa^{-1})
GaAs	10.89	11.4	−14.0[b]
GaP	9.11	7.4	−6.0[b]
ZnS	5.20	6.6	−2.6[c]
CdS (*c* axis)	5.38	9.1[d]	−11.0[e]
CdS (*a* axis)	5.31	8.3[d]	−10.8[e]
C	5.71	1.0	−1.1[f]
Si	11.97	7.8	−2.8[g]
Ge	16.00	13.8	−34.0[g]

[a] Unless otherwise noted, these values were deduced from the tabulation of $(d\ln n/dT)$ in Ref. 15.

[b] From a tabulation of $(d\ln n/dP)$ in Ref. 16.

[c] K. Vedam and E. D. D. Schmidt, Phys. Rev. 150, 766 (1966). The title of this paper mistakenly refers to α-ZnS which is the hexagonal wurtzite phase. However, the data in the paper are on sphalerite which is the cubic or β-ZnS phase.

[d] N. I. Vitrikhovskii, L. F. Gudymenko, and A. F. Maznichenko, Fiz. Tekh. Poluprovdn. 2, 882 (1968) [Soviet Phys.—Semicond. 2, 732 (1968)]. These derivatives were measured at $\lambda = 6907$ Å and we assume they are valid in the long-wavelength limit.

[e] K. Vedam and T. A. Davis, Phys. Rev. 181, 1196 (1969). These derivatives and those for ZnS were measured at $\lambda = 5893$ Å and we assume they are valid in the long-wavelength limit.

[f] D. F. Gibbs and G. J. Hill, Philos. Mag. 9, 367 (1964).

[g] R. Vetter, Phys. Status Solidi A 8, 443 (1971).

use in Table III and Sec. IV Vetter's[2] $n(P)$ data which appear to be more accurate than the data in Ref. 1.

We note here in passing that Smakula *et al.*[6] have reported the temperature dependence of ϵ of Si obtained from capacitance measurements. Their data show a monotonic decrease of ϵ with increasing T. This is in disagreement with the $n(T)$ data[1] which yield an increase in n (and ϵ) with increasing T. We believe that the $n(T)$ data represent the true response of Si. Additionally, by analogy with the behavior of Ge, C, and the other semiconductors in Table II, an increase (and not a decrease) of ϵ with increasing T can be expected for Si.

IV. ANALYSIS AND DISCUSSION

A. Lattice and electronic contributions

Before considering the results it is useful to examine some theoretical considerations. The real part of the dielectric function of a heteropolar semiconductor such as the compounds in Table II can be written as[12]

$$\epsilon = \epsilon_\infty + \frac{4\pi N e_T^{*2}}{\bar{m}\omega_{TO}^2} \qquad (1a)$$

$$\equiv \epsilon_\infty + \epsilon_l , \qquad (1b)$$

where ϵ is the static dielectric constant in the limit of zero frequency, ϵ_∞ is the high-frequency or optical (electronic) dielectric constant measured for frequencies well above the long-wavelength longitudinal-optic—mode frequency but below the optical-absorption edge, i.e., the dielectric constant in the absence of lattice vibrations, N is the number of unit cells per unit volume, $\bar{m}$ is the reduced mass of the crystal, e_T^* is the transverse dynamic effective charge, and ω_{TO} is the long-wavelength transverse-optical (TO)-mode frequency. The second term on the right-hand side of Eqs. (1) is the lattice contribution ϵ_l which arises because the longitudinal-optic (LO) mode in heteropolar semiconductors produce a macroscopic electric moment which separates it in energy from the TO mode. The frequencies of these modes are related to the dielectric constants by the Lyddane-Sachs-Teller relation

$$\epsilon/\epsilon_\infty = \omega_{LO}^2/\omega_{TO}^2 . \qquad (2)$$

With the use of the known values of ω_{LO}, ω_{TO}, ϵ, and ϵ_∞ given in Tables I—III, we find that this relation is very well obeyed for GaAs, GaP, and ZnS. Appreciable deviations are observed for CdS.

For homopolar crystals such as Si and Ge where there is a center of inversion symmetry between the atoms, $\omega_{LO} = \omega_{TO}$, and the lattice vibrations make no contribution to ϵ, so that

$$\epsilon=\epsilon_\infty \tag{3a}$$

$$\equiv n^2 , \tag{3b}$$

where n is the index of refraction.

ϵ_∞ is the strictly electronic contribution to ϵ. Expressions for $\epsilon_\infty(q)$ have been derived for various models of a semiconductor. The results are usually quite complicated depending on a knowledge of the energies of the allowed electronic states $E(k)$ and of the matrix elements for transitions between these states. The situation is simplest for $\epsilon_\infty(0)$, i.e., in the limit of long λ. van Vechten[13] has found that $\epsilon_\infty(0)$ of covalent crystals can be treated successfully by using a simple isotropic one-gap model (the Penn model) for the electronic band structure. The result is

$$\epsilon_\infty(0)=1+D(\omega_p/\omega_g)^2 , \tag{4}$$

where ω_p is the plasma frequency of the valence electrons, D is a parameter introduced by van Vechten to take into account the effect of d-like core electrons, and ω_g is the Penn gap. The temperature and pressure dependences of $\epsilon_\infty(0)$ have been successfully discussed in terms of the temperature and pressure dependences of ω_g via Eq. (4), and they have also been calculated using pseudopotential techniques.[14–17] For these purposes we note that $\omega_p^2=4\pi(Ze)^2/m\Omega$, where Ze is the charge and Ω is the atomic volume.

From Eq. (1b) it is evident that ϵ_l and its temperature and pressure dependences can be readily obtained from knowledge of $\epsilon(T,P)$ and $\epsilon_\infty(T,P)$. It is easily shown that

$$\left[\frac{\partial \ln\epsilon}{\partial T}\right]_P=\left[\frac{\epsilon_\infty}{\epsilon}\right]\left[\frac{\partial \ln\epsilon_\infty}{\partial T}\right]_P+\left[\frac{\epsilon_l}{\epsilon}\right]\left[\frac{\partial \ln\epsilon_l}{\partial T}\right]_P , \tag{5}$$

with a similar expression for the pressure derivatives. The decomposition of ϵ and its temperature and pressure derivatives into their electronic and lattice contributions are presented in Tables II–IV. Reference to these tables shows that for the compound semiconductors listed ϵ is dominated by the electronic contribution ϵ_∞; the lattice contribution ϵ_l is considerably smaller. The logarithmic temperature and pressure derivatives of ϵ_l are considerably larger than the corresponding derivative of ϵ and ϵ_∞, but this reflects in part the relatively small values of ϵ_l. The results in the tables also clearly show that the pressure dependence of ϵ_l is responsible for the anomalous increases of ϵ with pressure for a- and c-cut CdS. ϵ_∞ exhibits a normal response (decrease with pressure) for both orientations.

B. Macroscopic treatment

From the macroscopic point of view it is useful, as is quite common, to discuss the dielectric constants in terms of the electrical polarizability α of the medium. Here it should be remembered that unlike the case of ionic crystals where the effective electric field $E_{\text{eff}}=E+(4\pi/3)\mathscr{P}$, for the semiconductors of interest E_{eff} should be essentially equal to the macroscopic field E, i.e., $E_{\text{eff}}\approx E$.[12] This is because for these materials the outer electrons of the atoms have extended wave functions in both the ground and excited states and are therefore acted upon by the average macroscopic field.[18] This form of E_{eff} leads to the following expression for ϵ (Ref. 19):

$$\epsilon-1=4\pi(\alpha/V) , \tag{6}$$

where V is the volume. The logarithmic pressure and temperature derivatives of this expression are

$$\frac{\epsilon}{(\epsilon-1)}\left[\frac{\partial \ln\epsilon}{\partial P}\right]_T=\kappa-\kappa\left[\frac{\partial \ln\alpha}{\partial \ln V}\right]_T , \tag{7}$$

TABLE IV. Room-temperature (300-K) values of the lattice contribution (ϵ_l) to the static dielectric constant and its logarithmic temperature and pressure derivatives for the compound semiconductors of present interest. Data were deduced from the information in Tables II and III via Eqs. (1) and (5). Also listed are the calculated [using Eq. (1)] 300-K values of the transverse dynamic effective charge e_T^* expressed in units of the electronic charge e.

	ϵ_l	$(\partial\ln\epsilon_l/\partial T)_P$ (10^{-5} K^{-1})	$(\partial\ln\epsilon_l/\partial P)_T$ (10^{-3} GPa^{-1})	e_T^*/e
GaAs	2.24	64.4	−39.3	2.32
GaP	2.00	29.6	−32.7	2.06
ZnS	3.1	18.6	−24.8	2.02
CdS (c axis)	4.83	36.6	40.4	2.61
CdS (a axis)	3.68	33.6	25.1	2.35

$$\frac{\epsilon}{(\epsilon-1)}\left[\frac{\partial\ln\epsilon}{\partial T}\right]_P=-\beta+\beta\left[\frac{\partial\ln\alpha}{\partial\ln V}\right]_T+\left[\frac{\partial\ln\alpha}{\partial T}\right]_V, \tag{8}$$

where κ ($\equiv -\partial\ln V/\partial P$) is the volume compressibility and β ($\equiv\partial\ln V/\partial T$) is the volume thermal-expansion coefficient. The left-hand sides of these equations simply represent the fractional change in the quantity $(\epsilon-1)$ with pressure and temperature. It is seen that the pressure dependence of ϵ consists of two contributions. The first contribution, κ, represents the effect due to change in density and it makes ϵ increase with pressure. The second contribution is due to the change of the polarizability with pressure, or volume, and its sign depends on the sign of $\partial\ln\alpha/\partial\ln V$.

The temperature dependence of ϵ consists of three contributions; the first two constitute the total volume effect whereas the third contribution is the pure-temperature effect, i.e., the effect that would be present when the volume of the crystal is held constant. As we shall see later, this effect, which arises from anharmonicities in crystal potentials, is by far the most dominant contribution to the temperature dependences of both the electronic and lattice dielectric constants for the semiconductors in this paper. This is very much unlike normal ionic and molecular crystals where the volume effects dominate.[19]

Table V shows the separation of the pressure dependence of the dielectric constant into its two contributions. First we examine ϵ_∞ for the materials of interest as well as for Ge and diamond. As mentioned earlier, the pressure dependences of ϵ_∞ are taken from the literature. Note that in all cases the observed sign and magnitude of the pressure dependence of ϵ_∞ are dominated by the change in optical polarizability with pressure (or volume), a fact that has not always been appreciated before[20]—a change which more than counterbalances the effect due to the change in density. The quantity $\partial\ln\alpha/\partial\ln V$ represents the fractional change in α_∞ with fractional change in volume, and it is a positive quantity for all the materials in question, i.e., α_∞ increases (decreases) with increasing (decreasing) volume. This is what one expects intuitively: The distortion of the electronic cloud of an atom in an electric field (i.e., its electronic polarizability α_∞) becomes smaller when the space available for distortion (i.e., the volume) becomes smaller.

A qualitatively similar result is found for the lattice dielectric constants of GaAs, GaP, and ZnS (Table V). In these cases the decrease in ϵ_l with pressure results from the decrease in lattice polariza-

TABLE V. Separation of the pressure dependences of the electronic (ϵ_∞) and the lattice (ϵ_l) dielectric constants into their two contributions according to Eq. (7).

	$\frac{\epsilon}{\epsilon-1}\left[\frac{\partial\ln\epsilon}{\partial p}\right]_T=\kappa-\kappa\left[\frac{\partial\ln\alpha}{\partial\ln V}\right]_T$ (10^{-3} GPa^{-1})	$\left[\frac{\partial\ln\alpha}{\partial\ln V}\right]_T$
ϵ_∞		
GaAs	$-15.40=13.38-28.78$	2.15
GaP	$-6.72=11.28-18.00$	1.60
ZnS	$-3.22=12.78-16.00$	1.25
CdS[a] (*c* axis)	$-13.53=16.60-29.69$	1.82
CdS[a] (*a* axis)	$-13.33=16.60-29.45$	1.80
C	$-1.33=2.19-3.52$	1.61
Si	$-3.05=10.20-13.25$	1.30
Ge	$-36.38=13.29-49.67$	3.74
ϵ_l		
GaAs	$-69.95=13.38-83.33$	6.23
GaP	$-65.40=11.28-76.68$	6.80
ZnS	$-36.70=12.78-49.48$	3.87
CdS[a] (*c* axis)	$+50.90=16.60+34.30$	-2.07
CdS[a] (*a* axis)	$+34.40=16.60+17.80$	-1.07

[a] Equation (7) is strictly valid only for cubic crystals and the separation for hexagonal CdS should be viewed with caution [see P. S. Peercy, I. J. Fritz, and G. A. Samara, J. Phys. Chem. Solids 36, 1105 (1975)].

bility, or alternatively, from the stiffening of the lattice, i.e., increase in $\omega_{\rm TO}$ with pressure. This is the usual behavior and is seen in many dielectrics.[19] It can be understood by reference to Eq. (1a), where ϵ_l is expressed in terms of N ($\propto 1/V$), $e_{\rm T}^*$, and $\omega_{\rm TO}$. As we shall see later, the pressure dependence of $\omega_{\rm TO}^*$ determines that of ϵ_l.

The behavior of CdS is clearly anomalous. Here again the pressure dependence of ϵ_l is dominated by the pressure dependence of the polarizability, but in this case the polarizability increases with decreasing volume—that is what the negative $(\partial \ln\alpha/\partial \ln V)_T$ means. This can be interpreted microscopically via Eq. (1a) as resulting from a decrease (i.e., softening) of $\omega_{\rm TO}$ and/or an increase in $e_{\rm T}^*$ with increasing pressure (see subsection C below) for each crystal orientation. Unfortunately, the pressure dependences of the long-wavelength TO modes in CdS apparently have not been measured. A softening of the TO modes with pressure could be related to the presence of a pressure-induced phase transition in CdS at $\sim$2.5 GPa. Earlier studies have shown that all of the shear elastic constants of CdS soften with pressure on approaching the transition.[21] Since CdS is piezoelectric, coupling can be expected between the transverse-acoustic modes and the optic modes of the same symmetry. Specifically then, the decrease in ϵ_{11} with pressure could result (at least in part) from the associated TO mode being pulled down in frequency by the C_{44} acoustic mode, as the latter softens with pressure. ϵ_{33} does not couple piezoelectrically to any principal acoustic modes, but its increase with pressure could also be partly due to a softening of the associated TO mode brought about by the phase transition.

Table VI shows the contributions to the isobaric temperature dependences of ϵ_∞ and ϵ_l. We note that in all cases the two volume contributions (that due to the change in density β and that due to the change of α with volume) are relatively small and tend to partially cancel each other. In the case of ϵ_l of CdS these two effects have the same sign for the reasons discussed above. The most striking feature of the results in Table VI is the overwhelming dominance of the volume-independent, or pure-temperature, contribution $(\partial \ln\alpha/\partial T)_V$ for both ϵ_∞ and ϵ_l. This has been recognized for Si and Ge (Ref. 1) and a similar result is found for the temperature dependence of many energy levels in semiconductors.[22,23] The contribution $(\partial \ln\alpha/\partial T)_V$ is absent in standard (harmonic) theory, and it arises from anharmonicities in crystal potentials. For ϵ_∞ the anharmonicities are due to electron-phonon interactions, while for ϵ_l they are due to interactions among phonons. These anharmonicities continue to be topics of considerable interest, but their origin and sign are not well understood on a microscopic scale. For the electron-phonon interaction empirical

TABLE VI. Separation of the temperature dependences of the electronic (ϵ_∞) and lattice (ϵ_l) dielectric constants into their various contributions according to Eq. (8). All quantities are in units of (10^{-5} K^{-1}).

	$\frac{\epsilon}{\epsilon-1}\left(\frac{\partial \ln\epsilon}{\partial T}\right)_P = -\beta+\beta\left(\frac{\partial \ln\alpha}{\partial \ln V}\right)_T + \left(\frac{\partial \ln\alpha}{T}\right)_V$
ϵ_∞	
GaAs	12.54 = −1.71 + 3.68 + 10.57
GaP	8.29 = −1.59 + 2.54 + 7.34
ZnS	8.18 = −2.01 + 2.51 + 7.67
CdS[a] (*c* axis)	11.20 = −1.25 + 2.28 + 10.17
CdS[a] (*a* axis)	10.20 = −1.25 + 2.26 + 9.19
C	1.21 = −0.33 + 0.53 + 1.01
Si	8.50 + −0.75 + 0.98 + 8.27
Ge	14.77 = −1.71 + 6.46 + 10.02
ϵ_l	
GaAs	114.63 = −1.71 + 10.65 + 105.69
GaP	59.20 = −1.59 + 10.81 + 49.98
ZnS	27.53 = −2.01 + 7.78 + 21.76
CdS[a] (*c* axis)	46.00 = −1.25 − 2.59 + 49.84
CdS[a] (*a* axis)	46.00 = −1.25 − 1.34 + 48.59

[a] Equation (8) is strictly valid only for cubic crystals and the separation for hexagonal CdS should be viewed with caution (see reference in footnote to Table V).

pseudopotential calculations have had some success.[14,15,22]

Examination of Table VI reveals an interesting quantitative feature. The pure-temperature contribution $(\partial \ln \alpha / \partial T)_V$ associated with $\epsilon_\infty(T)$ has nearly the same value for GaAs and Ge which are isoelectronic. This may be purely coincidental or it may suggest that the electron-phonon interaction may be similar for isoelectronic sequences in semiconductors of diamond and zinc-blende structure despite large differences in their electronic and phonon structure.

C. Effective charge and its pressure dependence

As can be seen from Eq. (1), from the microscopic point of view, the lattice contribution to the dielectric constant ϵ_l is determined by the long-wavelength ($\vec{q}=0$) TO-phonon frequency $\omega_{\rm TO}$ and the transverse dynamic effective charge $e_{\rm T}^*$ in addition to the density and the reduced mass of the crystal. All of the quantities in Eq. (1) are either measurable or known except $e_{\rm T}^*$.[24] $\omega_{\rm TO}$ values have been reported for GaAs, GaP, ZnS, and CdS and are given in Table I. These values, combined with the present results on ϵ_l, allow us to calculate $e_{\rm T}^*$ for these crystals. Our calculated values of $e_{\rm T}^*$ given in Table IV agree well with earlier[12,25] determinations of this quantity.

From Eq. (1) it follows that

$$\left(\frac{\partial \ln \epsilon_l}{\partial p}\right)_T = \kappa + 2\left(\frac{\partial \ln e_{\rm T}^*}{\partial p}\right)_T - 2\left(\frac{\partial \ln \omega_{\rm TO}}{\partial p}\right)_T . \tag{9}$$

The pressure dependence of $\omega_{\rm TO}$ has been reported for GaAs (Ref. 26) and GaP.[27] Table VII analyzes the room-temperature pressure dependences of ϵ_l of these two crystals according to Eq. (9).

TABLE VII. Decomposition of the pressure dependence of ϵ_l at 300 K into its various contributions according to Eq. (9) for GaAs and GaP.

	$\left(\frac{\partial \ln \epsilon_l}{\partial P}\right)_T = \kappa + 2\left(\frac{\partial \ln e_{\rm T}^*}{\partial P}\right)_T - 2\left(\frac{\partial \ln \omega_{\rm TO}}{\partial P}\right)_T$ (10^{-3} GPa^{-1})
GaAs	$-39.3=13.4-15.5-37.2$[a]
GaP	$-32.7=11.3-19.4-24.6$[b]

[a] From Ref. 26.

[b] From Ref. 27.

The results in Table VII show that whereas for these crystals the decrease in ϵ_l with pressure is dominated by the increase in $\omega_{\rm TO}$ with pressure, the contribution from the pressure dependence of $e_{\rm T}^*$ is quite substantial. For GaP this contribution is of nearly the same magnitude as that from the $\omega_{\rm TO}$ term. We also note that $e_{\rm T}^*$ decreases with pressure for both crystals.

The increase in $\omega_{\rm TO}$ with pressure is intuitively expected since as the interatomic distances become shorter with pressure the lattice should become stiffer. The pressure dependence of $e_{\rm T}^*$, on the other hand, is not so easily visualized. For highly covalent crystals such as GaAs and GaP, the static ionic charge should be small. The relatively large calculated values of $e_{\rm T}^*$ ($>2e$, where e is the electronic charge) are not a measure of this static charge, but, rather, reflect the dynamic effective charge which results from a redistribution or transfer of charge between the two kinds of atoms in the course of TO lattice vibrations. They are a measure of the highly polar character of the TO modes in III-V compound semiconductors. These charges are $\sim\frac{2}{3}$ of what the static charges would be were these crystals fully ionic (the normal valence is equal to 3 for III-V compounds). The decrease of $e_{\rm T}^*$ with pressure for GaAs and GaP implies less transfer of charge for the compressed crystal, i.e., the character becomes more covalent.

In ZnS, CdS, and other II-VI compound semiconductors the bonding is less covalent (or more ionic) than in III-V compounds. This is reflected in the calculated values of $e_{\rm T}^*$ for ZnS and CdS in Table IV ($\gtrsim 2e$) which are comparable to (for ZnS) or greater (for CdS) than what the static charges would be were these crystals fully ionic (normal valence is equal to 2 for II-VI compounds). Apparently the pressure dependences of the $\omega_{\rm TO}$'s for cubic ZnS and hexagonal CdS have not been reported, and it is thus not possible to calculate the pressure dependences of the $e_{\rm T}^*$'s using Eq. (9). The often-quoted[26] value

$$\gamma_{\rm TO} \equiv -\left(\frac{\partial \ln \omega_{\rm TO}}{\partial \ln V}\right)_T = 1.8-2.0$$

for the Grüneisen parameter of the TO mode of ZnS appears to be for the hexagonal and not the cubic phase of this crystal.[28] Use of this value in Eq. (9) would yield an increase in $e_{\rm T}^*$ with pressure which, in view of the present results on GaAs and GaP and earlier results on other crystals,[28] is not likely. According to Eq. (9), $\gamma_{\rm TO}$ for cubic ZnS would have to be less than 1.47 to yield the expected decrease of $e_{\rm T}^*$ with pressure.

The pressure dependence of $e_{\rm T}^*$ of GaAs has been recently reported by Trommer *et al.*[26] based on their measurement of the pressure dependences of $\omega_{\rm TO}$ and $\omega_{\rm LO}$ (the longitudinal-optic-mode frequency) and the known pressure dependence of ϵ_∞. They employed the expression

$$e_T^{*2} = \left[\frac{\bar{m}}{4\pi N}\right]\epsilon_\infty(\omega_{\mathrm{LO}}^2-\omega_{\mathrm{TO}}^2) \,. \tag{10}$$

It is easily shown by using Eq. (2) that this form of the expression for e_T^* is equivalent to that in our Eq. (1). Their results yield an initial slope

$$\left[\frac{\partial \ln e_T^*}{\partial p}\right] = -8.4\times 10^{-3}$$

(in units of GPa^{-1}), which compares favorably with our value of $-7.8\times 10^{-3}\ \mathrm{GPa}^{-1}$.

With the use of estimates of the pressure dependence of ϵ_∞, Weinstein and Zallen[28] recently calculated the pressure dependences of e_T^* for several zinc-blende crystals on the basis of Eq. (10). Their results yield $(\partial \ln e_T^*/\partial p) = -6.7$ and -5.7 $(\times 10^{-3}\ \mathrm{GPa}^{-1})$ for GaAs and GaP, respectively. The value for GaP is considerably smaller than our result in Table VII.

Earlier Mitra and Namjoshi[29] reported the pressure dependence of the Szigeti effective charge e_S^* for GaP.[24] Their result, based on the then available pressure dependences of ω_{TO} and ω_{LO}, and assuming $d\epsilon_\infty/dP=0$, yielded an increase in e_S^* with pressure. This increase in e_S^* with pressure was based largely on the then believed increase in the LO-TO—mode splitting with pressure. The more recent Raman scattering results[27] show that this splitting decreases with pressure, and this factor, along with the decrease in ϵ_∞ with pressure, should lead to a decrease in e_S^* as well as in e_T^* with pressure, as found in the present work.

Recent theoretical approaches used to calculate e_T^* of tetrahedral semiconductors have included the semiempirical bond-orbital model[30] and a pseudopotential model.[31] In both approaches the details of the calculations are quite complicated and strong simplifying assumptions are necessary to obtain the sign and order of magnitude of the observed effects.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the expert technical assistance of B. E. Hammons and to thank L. Ralph Dawson for providing the GaAs and GaP samples. I also thank B. A. Weinstein and R. Zallen for a copy of their review paper before publication. This work was performed at Sandia National Laboratories, which is supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

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