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Effect of Pressure on Interband Reflectivity Spectra of Germanium and Related Semiconductors*

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The pressure dependences of the position of peaks occurring between 2 and 5 eV in the reflectivity spectra of Ge, Si, GaSb, InSb, InAs, and GaP have been measured to 10 kbar, and the results taken to give the pressure coefficient of energy separations corresponding to direct interband transitions. Seven peaks between 2 and 3 eV, members of E_1, $E_1+\Delta_1$ doublets associated with $\Lambda_3^v \rightarrow \Lambda_1^c$ transitions, shift to higher energy at rates between $+6\times10^{-6}$ and $+9\times10^{-6}$ eV/bar. No pressure dependence of Δ_1, the spin-orbit splitting of the Λ_3^v valence band, was found within the experimental accuracy of $\pm1\times10^{-6}$ eV/bar. The dominant E_2 peak near 4 eV has a pressure coefficient of about $+6\times10^{-6}$ eV/bar for Ge, GaSb, and InSb, and $+3\times10^{-6}$ eV/bar for Si. The peaks at 3.4 eV in Si and 3.7 eV in GaP possess coefficients of $+5\times10^{-6}$ and $+6\times10^{-6}$ eV/bar, respectively. The addition of these data to earlier results on the pressure dependences of energy separations in this family of semiconductors modifies and extends a previously noted correlation between transition type and pressure coefficient. A comparison of the measured coefficients with recently reported calculations reveals considerable agreement, with the discrepancies suggesting that a reinterpretation is required for the E_2 peaks and, especially, for the peak at 3.4 eV in Si.

1. INTRODUCTION

A. General

THIS paper presents some new experimental results on the pressure dependence of the electronic energy band structure of group IV and group III-V semiconductors. Earlier work[1–6] on the effect of isotropic compression on the band structure of these cubic semiconductors (diamond structure for the elements, zincblende structure for the compounds) has been confined primarily to electronic states immediately adjacent to the forbidden gap. The present work yields information about the influence of pressure on several direct interband energy gaps in the 2–5-eV energy range, spanning the forbidden zone, and probes portions of the band structure a few eV deep into the valence and conduction bands.[7] The measurements were effected by exploiting the connection, discussed in the following section, which has been established between certain special direct energy gaps and the position (photon energy) of peaks appearing in the ultraviolet reflectivity spectra of these materials; the reflectivity peaks were treated as markers and their shift in position with hydrostatic pressure was used as a measure of the pressure dependence of the corresponding energy gaps.

The crystalline solids studied here, the covalent semiconductors of the germanium family, are among those for which the one-electron approximation most closely holds and the one-electron energy-band description is most appropriate. Like the zero-pressure band structure itself, the variation of the band structure with isotropic compression, which reduces their interatomic spacing while preserving their cubic crystal symmetry, is a fundamental property of these materials which must ultimately be accounted for theoretically. In very recent calculations of the band structure of silicon and germanium, Herman and co-workers[8] have compared their theoretical deformation potentials with our data in order to help resolve certain questions about the band structure of these materials; their conclusions are discussed in Secs. 4 B and 4 D.

B. Reflectivity Spectra and Interband Transitions

Since Philipp and Taft[9] first reported, in 1959, the strong structure between 1 and 10 eV in the reflectivity spectrum of germanium, the measurement of ultraviolet reflectivity spectra has developed into a powerful tool for the experimental investigation of electronic energy band structure in crystalline solids.[10–20] The

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[19] M. Cardona, in *Proceedings of the Seventh International Conference in the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 181.

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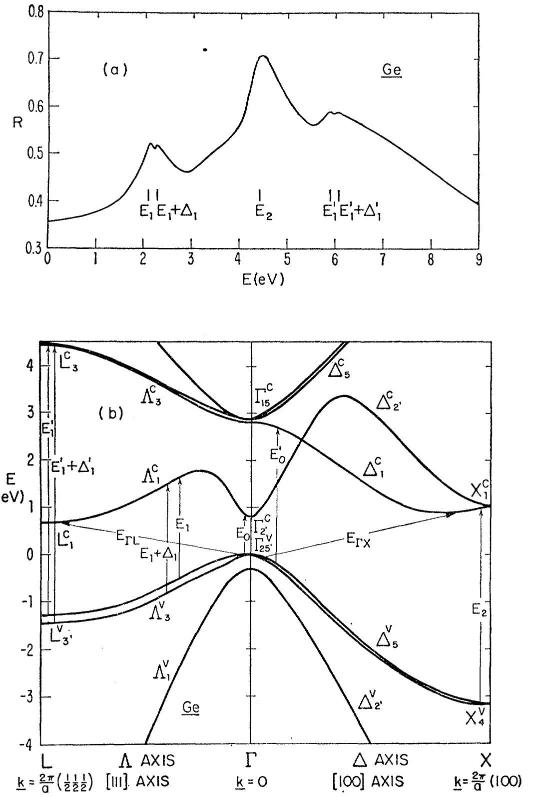

FIG. 1. (a) Reflectivity spectrum of germanium (see Refs. 9, 14, and 27); (b) band structure of germanium along two symmetry directions, including states within 4 eV of the valence-band maximum (see Refs. 8, 28, and 29).

original interpretation of the germanium data in terms of direct interband transitions was provided by Phillips.[10] Later, a comprehensive treatment of the description of optical properties by means of direct transitions was given by Brust.[18] The band structures of many materials have now been inferred from their reflectivity spectra. Compilations of the values of various reflectivity-determined direct energy gaps have been presented in reviews by Cardona[19] and by Phillips.[20] The most recent development in the technique is the use of stress-modulated[21] or electric-field-modulated[22] reflectivity; electroreflectivity in particular has proved to be a valuable extension of the method, as structure is sometimes found which does not appear, or which appears only very weakly, in the ordinary reflectivity. Although the shape of the modulated-reflectivity structure is not yet understood, the structure is quite sharp so that energies of interband transitions are accurately determined.[23] This clearly suggests a new approach to the determination of stress coefficients of interband energy gaps based on the modulated-reflectivity structure; work combining static uniaxial stress and electroreflectivity has been reported by Pollak, Cardona, and Shaklee[24] for GaAs.

The observed quantity in the reflectivity experiments is the spectral function $R(E)$, where R is the normal-incidence reflectivity at photon energy E. The information derived concerns the electronic energy-momentum spectrum $E_n(\mathbf{k})$, or band structure, in the one-electron picture. $E_n(\mathbf{k})$ is the energy eigenvalue for wave vector $\mathbf{k}$ and band index n. The connection between $R(E)$ and $E_n(\mathbf{k})$ is outlined briefly in the following two paragraphs. The detailed arguments may be found in the articles by Brust[18] and by Phillips.[17,20]

We assume that direct transitions dominate and that the magnitude of the interband matrix element varies little with $\mathbf{k}$ throughout the Brillouin zone. Then $\epsilon_2(E)$, the imaginary (absorptive) part of the complex dielectric constant at frequency $\nu=E/h$, is approximately proportional to $\rho_{cv}(E)/E^2$, where $\rho_{cv}(E)$ is the joint density of states for vertical transitions between states in the valence band at energy $E_v(\mathbf{k})$ and states in the conduction band at energy $E_c(\mathbf{k})=E_v(\mathbf{k})+E$. Structure appearing in $\rho_{cv}(E)$ will produce structure in $\epsilon_2(E)$ and, in turn, $R(E)$. Such corners (discontinuities in slope) of a density-of-states function may be described by means of the critical-point theory originally developed for the theory of lattice vibrations.[25] A critical point responsible for a corner in $\rho_{cv}(E)$ occurs when $\nabla_{\mathbf{k}}E_c(\mathbf{k})=\nabla_{\mathbf{k}}E_v(\mathbf{k})$, i.e., when the bands are parallel.[17,18] Thus, structure in $R(E)$ is correlated with special features of the valence- and conduction-band structures corresponding to the critical-point condition $\nabla_{\mathbf{k}}E_{cv}(k)=0$, where $E_{cv}(\mathbf{k})=E_c(\mathbf{k})-E_v(\mathbf{k})$.

In many cases, it then becomes possible to assign a peak in $R(E)$, occurring at photon energy E_i, to a particular direct transition (or equivalently, to a particular direct-interband energy gap) occurring at a critical point $\mathbf{k}_i$: $E_i=E_{cv}(\mathbf{k}_i)$. In general, $\mathbf{k}_i$ implies a set of symmetrically equivalent wave vectors, especially since critical points frequently occur at points of high symmetry, such as at the center or on the boundary of the Brillouin zone, where $\nabla_{\mathbf{k}}E_{cv}$ vanishes because $\nabla_{\mathbf{k}}E_c$ and $\nabla_{\mathbf{k}}E_v$ individually vanish. The association of a particular reflectivity peak with a particular set of critical points is reasonable only when the structure in $\rho_{cv}(E)$ is dominated by contributions from a small fraction of the volume of the zone confined to regions in the vicinity of the critical points. The recent papers by Kane[26] and by Herman *et al.*[8] demonstrate that much of the structure in $\rho_{cv}(E)$ and $R(E)$ is caused by an

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accumulation of contributions over an appreciable portion of the zone, so that the viewpoint presented above is an oversimplification. Indeed, as discussed in Sec. 4 D, the results of the present experiments are one indication of this complication. Nevertheless, it is convenient, although occasionally misleading, to associate the optical structure with particular transitions, and we shall do this in much of our discussion, making reference to the more complete picture when necessary.

The methods used for identifying specific direct transitions with specific reflectivity peaks include comparison with calculated band structures, presence or absence of spin-orbit or crystal-field splitting, alloy studies, systematic variations among related materials, and, of interest here, the measurement and comparison of pressure coefficients. The reflectivity-determined energy separations of roughly five to ten different direct transitions in about twenty different semiconductors of groups IV, III-V, II-VI, and I-VII are tabulated in Cardona's 1964 review article.[19]

C. Pressure Experiments

Figure 1 shows the ultraviolet reflectivity spectrum for germanium[9,14,27] as well as a portion of the current version of the band structure[8,28,29] along two lines of high symmetry from the center to the boundary of the Brillouin zone. The electronic states are labeled using the notation for the representations of the single group of the diamond structure.[30] The reflectivity peaks and energy separations corresponding to the vertical transitions are labeled with a convenient notation introduced by Cardona.[13] The transitions labeled E_1 and E_2 are the two of principal interest in this paper. The large E_2 peak is the dominant central peak exhibited by all of the group IV and group III-V semiconductors, usually in the vicinity of 4 or 5 eV. Brust's calculations[18] for both Ge and Si associate this structure with two nearly degenerate sets of critical points: at the X points, (100) on the zone boundary; and along the Σ lines ([110] axes) inside the zone. The E_1, $E_1+\Delta_1$ structure in Ge, first resolved as a doublet by Tauc and Antončik,[11] is assigned by Brust to $\mathbf{k}_i$ lying along the Λ lines ([111] axes) about one-third of the way out from the zone center; the splitting Δ_1 is the spin-orbit splitting of the $\Lambda_3{}^v$ valence band.

In the present work, we have measured the pressure dependence of E_2 peaks in Ge, Si, GaSb, and InSb; E_1 doublet peaks in Ge, GaSb, InSb, and InAs; and the low-energy singlet peaks in Si (3.4 eV) and GaP (3.7 eV). Experimental aspects are discussed in Sec. 2; the results obtained are presented in Sec. 3 and are discussed in Sec. 4. The E_2 and the E_1 doublet peaks are discussed in Sec. 4 A. The low-energy Si and GaP peaks, discussed separately in Sec. 4 B, have, in the past, been identified with an energy gap distinctly different from the E_1 energy separation which has been assigned to the strong low-energy peaks in all of the other group IV's and III-V's. Recent developments, in which the present pressure data play a role, suggest that this sharp distinction may not exist; these are discussed in Sec. 4 B. In Sec. 4 C we review the experimental information available to date on the pressure dependence of the band structure of semiconductors of groups IV and III-V, and in Sec. 4 D, we compare the Ge data with available band calculations. The latter comparison supports the contention of Kane[26] and of Herman *et al.*[8] that the large E_2 peak is not dominated by $X_4{}^v \rightarrow X_1{}^c$ transitions.

2. EXPERIMENTAL TECHNIQUES

The apparatus which we used to measure the effect of hydrostatic pressure on reflectivity spectra has been described previously,[6,29] so that only a few remarks about the experimental arrangement are needed here. Four etched samples were arranged in periscopelike fashion in a reflectivity cell and immersed in isopentane inside a high-pressure vessel equipped with two sapphire windows. In order for light to be "transmitted" by the reflectivity capsule, it had to undergo four 45° reflections from etched[31] surfaces of the material being studied. The purpose of using four reflections rather than a single one was twofold: (a) to permit the use of a straight-through geometry in which the experimentally measured quantity was the transmission of the reflectivity cell; and (b) to effectively sharpen the observed structure in the vicinity of the reflectivity peaks. Because the materials under investigation were optically isotropic, and, of course, remain so under isotropic compression, polycrystalline samples, if necessary, and unpolarized light could be used in these experiments. All measurements were performed at room temperature. The maximum pressure used was 10 kbar.

Typical experimental results are shown in Fig. 2, in which the transmission of a Ge reflectivity cell in the vicinity of the E_1, $E_1+\Delta_1$ doublet is plotted against photon energy ($h\nu$) at various pressures. The insert at the upper right corner schematically indicates the cell geometry. The curves have been vertically displaced in order to separate them from each other for clarity; the vertical scale (arbitrary units) is indicated only for the top and bottom curves.

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[27] T. M. Donovan, E. J. Ashley, and H. E. Bennett, J. Opt. Soc. Am. **53**, 1403 (1963); P. Grant, Technical Report No. HP-14, Gordon McKay Laboratory of Applied Science, Harvard University, 1965 (unpublished).

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[30] H. Jones, *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960).

[31] The polishing and etching procedures used here are described in Sec. 2D of Ref. 29. As has been frequently pointed out by other workers, it was invariably found that chemical etching was required for removing the damage layer produced by mechanical polishing, in order to reveal the characteristic structure in the reflectivity spectra.

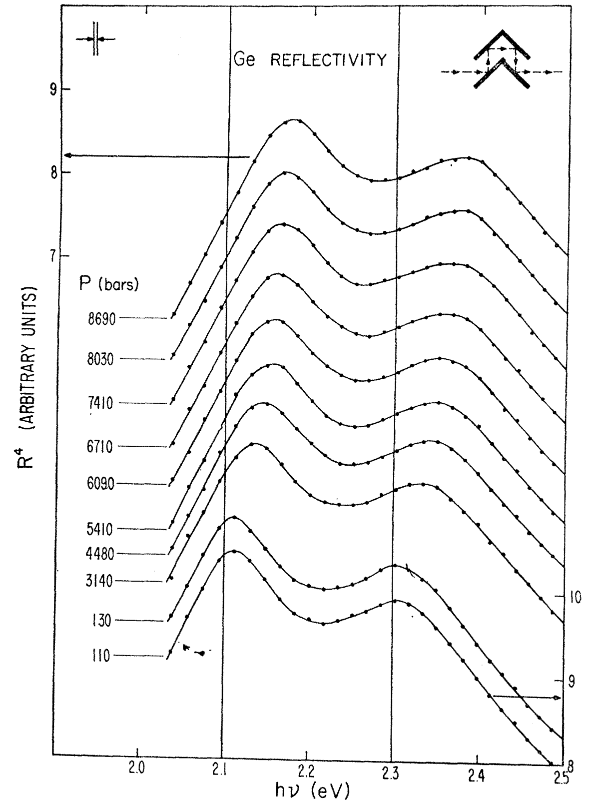

FIG. 2. The effect of pressure on the Ge reflectivity peaks at 2.1 and 2.3 eV. (The insert at the upper right schematically portrays the sample geometry.)

A brief discussion of the ordinate, labeled R^4, used in Fig. 2, is in order, since R is normally reserved for the reflectivity at normal incidence in air, given by

$$\frac{(n-1)^2+K^2}{(n+1)^2+K^2},$$

n and K being the refractive index and the extinction coefficient, respectively, of the solid. Let t represent the transmission of the reflectivity cell, and let $R_\perp$ and $R_\parallel$ represent the reflectivities for light polarized perpendicular and parallel, respectively, to the plane of incidence. For unpolarized incident light, $t=\frac{1}{2}R_\perp{}^4+\frac{1}{2}R_\parallel{}^4$. At 45° incidence, $R_\parallel=R_\perp{}^2$, so that $t=\frac{1}{2}R_\perp{}^4(1+R_\perp{}^4)$. Since $R_\perp$ is here typically about 0.6, then $R_\perp{}^4\sim 0.1$ and, to a close approximation, t is simply proportional to $R_\perp{}^4$. For light incident at angle θ upon an interface between a transparent liquid having refractive index n' and a solid having optical constants n and K, we have

$$R_\perp=\frac{(n-n'\cos\theta)^2+K^2}{(n+n'\cos\theta)^2+K^2},$$

in the limit in which $n^2+K^2\gg n'^2$.[32] In our situation, $n^2+K^2\approx 30$, and $n'^2\approx 2$ so that this expression applies fairly well. Furthermore, for the particular combination of n' and θ appropriate here ($n'\approx 1.4$ for isopentane, $\theta=45°$), it turns out that $n'\cos\theta$ is very close to unity, so that the expression for $R_\perp$ is very nearly equal to $[(n-1)^2+K^2]/[(n+1)^2+K^2]$, the expression for R. Thus the peak positions for the low-pressure curves of Fig. 2 are expected to closely correspond to those found by other workers for $n'=1$ and $\theta=0$ (normal incidence in air); this was indeed the case (agreement to within about 0.02 eV).

Since the object of these measurements was to determine the shift with pressure of the reflectivity peaks resulting from the pressure dependence of $n(h\nu,P)$ and $K(h\nu,P)$, it was necessary to ascertain to what extent the pressure-dependent refractive index of the pressure fluid, $n'(h\nu,P)$, influenced an observed shift such as that shown in Fig. 2. Using the knowledge that n' is a very slowly varying function of $h\nu$ in comparison with n and K, and that n'^2 is much smaller than n^2+K^2, one can conclude, with the aid of the expressions discussed above, that this effect is unimportant in the present case. Direct experimental evidence for this was provided by the observation that the shift in the positions of the reflectivity-cell transmission maxima produced by replacing air ($n'=1.00$) by isopentane at low pressure ($n'=1.36$) was, when discernible, slight in comparison with the subsequent shift induced by pressure. Since increasing n' from 1.00 to 1.36 has a negligible effect on

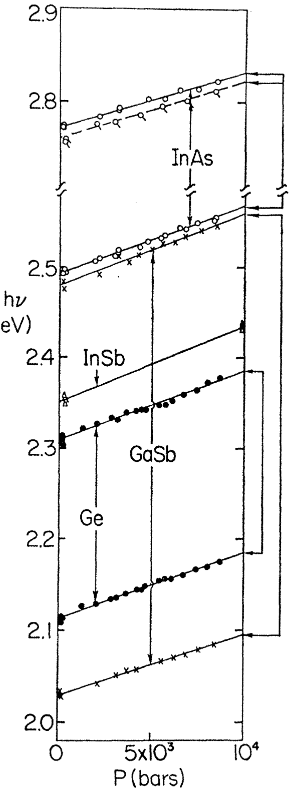

FIG. 3. The pressure dependence of the position of doublet reflectivity peaks for Ge, GaSb, InAs, and InSb.

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[32] R. W. Ditchburn, *Light* (Interscience Publishers, Inc., New York, 1953), p. 444.

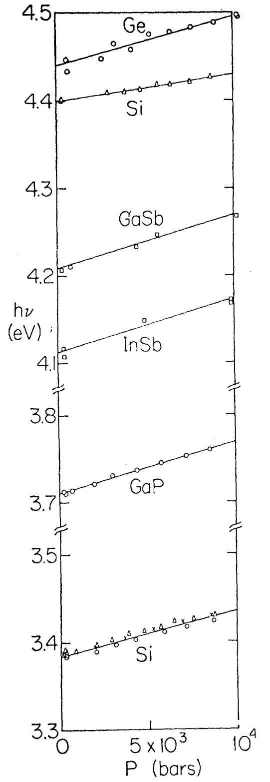

FIG. 4. The pressure dependence of the position of reflectivity peaks for Ge, Si, InSb, GaSb, and GaP.

peak position, the additional increase to 1.50 at 10 kbar (calculated by means of the Clausius-Mosotti relation and Bridgman's compressibility data[33]) would also have negligible effect. Thus no correction for $n'(P)$ is needed in this instance.[34]

From the above discussion we conclude that results such as those shown for Ge in Fig. 2 may be directly attributed to the pressure dependence of the optical constants of the semiconductor, and, in turn, to the pressure dependence of the direct-interband energy gaps responsible for the structure in the optical properties.

3. RESULTS

We have measured the effect of pressure on 13 reflectivity peaks, spanning the range of photon energy between 2.0 and 4.5 eV, in the family of semiconductors of groups IV and III-V. All of the energy gaps studied in this way were observed to increase with pressure. The peaks studied were those at 2.1, 2.3, and 4.5 eV in Ge; 2.0, 2.5, and 4.2 eV in GaSb; 2.5 and 2.8 eV in InAs; 2.4 and 4.1 eV in InSb; 3.4 and 4.4 eV in Si; and 3.7 eV in GaP. Of the 13 peaks measured, the 7 lowest in energy (between 2.0 and 2.8 eV) are members of E_1, $E_1+\Delta_1$ doublets, while the four highest in energy (between 4.1 and 4.5 eV) are the dominant E_2 peaks. The other two peaks, at 3.4 eV in Si and at 3.7 eV in GaP, are singlet peaks requiring separate discussion, because their interpretation has varied with time and is less clearly established.

The pressure dependence of the E_1, $E_1+\Delta_1$ peaks studied is shown in Fig. 3. Both members of the doublet were measured for Ge, GaSb, and InAs; only the $E_1+\Delta_1$ member was measured for InSb. (The two curves shown for the upper InAs peak are results obtained from different samples; although slightly displaced in energy, the two curves reveal the same pressure dependence.)

Figure 4 displays the pressure dependence of the six higher-energy reflectivity peaks studied. The four upper curves in Fig. 4 show the shift with pressure of the large E_2 peaks in Ge, Si, GaSb, and InSb; the two lower curves show the pressure shift of the low-energy Si and GaP peaks.

The pressure coefficients corresponding to the slopes of the curves of Figs. 3 and 4 are listed in Table I and are discussed in the following sections.

4. DISCUSSION

A. The E_2 Peaks and E_1 Doublet Peaks

The seven E_1-type energy gaps shown in Fig. 3 all increase with pressure at nearly the same rate; the corresponding pressure coefficients listed in Table I fall between $+6\times10^{-6}$ and $+9\times10^{-6}$ eV/bar. The spin-orbit splitting of the $\Lambda_3{}^v$ valence band, Δ_1, does not exhibit a pressure dependence within the accuracy of the present measurements, which is of the order of $\pm1\times10^{-6}$ eV/bar.

The rates at which the four large E_2 peaks shift in energy with pressure are given in the last column of Table I. An interesting feature of this group of coefficients is that the silicon coefficient of $+3\times10^{-6}$ eV/bar is markedly lower than the others, which are about $+6\times10^{-6}$ eV/bar. The E_2 coefficients for Ge and Si are discussed further in Sec. 4 D.

TABLE I. Measured pressure coefficients of direct interband energy gaps.

	Reflectivity peak positions in eV			Pressure coefficients in 10^{-6} eV/bar		
Material	E_1	$E_1+\Delta_1$	E_2	$\frac{dE_1}{dP}$	$\frac{d(E_1+\Delta_1)}{dP}$	$\frac{dE_2}{dP}$
Ge	2.11	2.31	4.44	7.5±0.5	7.6±1.0	5.6±1.0
GaSb	2.03	2.48	4.21	6.5±0.5	8.2±1.0	6.2±1.0
InAs	2.49	2.77		7.4±0.5	6.3±1.0	
InSb		2.35	4.12		8.5±1.0	5.8±1.0
Si	3.38[a]		4.4	5.2±0.5		2.9±0.5
GaP	3.71[a]			5.8±1.0		

[a] The identification of this peak is not well established; it is listed as E_1 for convenience. See discussion in Sec. 4 B.

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[33] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **66**, 185 (1931).

[34] This is in contrast to an analogous measurement, cited below, on the pressure dependence of the reflectivity edge in silver at 3.8 eV. For the metal, $n\sim K\sim1\sim n'$ in the vicinity of the effective plasma edge, and an explicit correction for $n'(P)$ was required in order to accurately determine the small pressure coefficient of this edge. R. Zallen, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland Publishing Company, Amsterdam, 1966), p. 164.

Two of the pressure coefficients reported here can be directly compared with dilational deformation-potential differences deduced by Gerhardt[35] from his very careful static piezoreflectivity measurements on germanium and silicon. This net deformation potential corresponds to $dE/d\ln V$, and is simply related to the corresponding pressure coefficient through the volume compressibility K:

$$\frac{dE}{d\ln V}=-\frac{1}{K}\frac{dE}{dP}.$$

Gerhardt obtains values of this deformation potential for the 2.1-eV peak in Ge and the 4.4-eV peak in Si as follows: Ge E_1 peak, (-5.7 ± 0.3) eV; Si E_2 peak, (-2.7 ± 0.5) eV. The pressure coefficients we obtain for these energy gaps are $(+7.5\pm0.5)\times10^{-6}$ eV/bar and $(+2.9\pm0.5)\times10^{-6}$ eV/bar, corresponding to deformation potentials of (-5.7 ± 0.4) and (-2.9 ± 0.5) eV, respectively, in excellent agreement with Gerhardt's results.

B. The Low-Energy Singlet Peaks in Si and GaP

The silicon reflectivity peak at 3.4 eV is an interesting case because it has been thought to be of substantially different origin than the E_1 peaks of Fig. 3.[13–20] The main experimental arguments which have been given for this view have been the chemical-shift data of Tauc and Abraham[12] on Ge-Si alloys and the Si piezoreflectivity measurements of Gerhardt,[35] while the theoretical basis has been provided by pseudopotential band calculations.[18,36] (The lack of observed doublet structure is not a part of the argument, since the valence-band spin-orbit splitting in Si is quite small.) Tauc and Abraham followed the position of the first reflectivity peak as a function of composition in the alloy system and found a definite break at about $\mathrm{Ge}_{0.2}\mathrm{Si}_{0.8}$, indicating, by analogy with the absorption-edge alloy data,[37] different transitions for the low-energy peaks in Ge and Si. In his initial calculations, Brust[18] assigned the Si peak to $\Gamma_{25'}{}^{v}\rightarrow\Gamma_{15}{}^{c}$ transitions at the zone center; in a later treatment,[36] he associated it with $\Delta_5{}^{v}\rightarrow\Delta_1{}^{c}$ transitions along the [100] axes in the vicinity of the Γ point. The latter assignment is consistent with conclusions arrived at by Gerhardt[35] from his careful measurements of the polarization-dependent reflectivity of bent single crystals. Gerhardt found that [111] stress shifts the peak equally for both polarizations of incident light, while [100] stress splits the peak into two polarization-dependent components, behavior strongly suggestive of Δ symmetry for the underlying transitions. E_0' is used to denote the energy separation corresponding ro $\Gamma_{25'}{}^{v}\rightarrow\Gamma_{15}{}^{c}$, or nearby $\Delta_5{}^{v}\rightarrow\Delta_1{}^{c}$, transitions.

However, the above interpretation has been strongly questioned by Herman *et al.*[8] on the basis of their recent detailed calculations for Si. Herman's arguments that the Si 3.4-eV peak cannot be assigned to E_0' are twofold: (a) His new theoretical estimate of the $\Gamma_{25'}{}^{v}\rightarrow\Gamma_{15}{}^{c}$ gap is (2.8 ± 0.1) eV, rather than 3.4 eV; (b) his calculated pressure coefficient for energy separations along the Δ axis varies between $+0.6\cdot10^{-6}$ eV/bar (at the zone center, $\Gamma_{25'}{}^{v}\rightarrow\Gamma_{15}{}^{c}$) and $+1.4\cdot10^{-6}$ eV/bar (at the zone boundary, $X_4{}^{v}\rightarrow X_1{}^{c}$), being everywhere very much smaller than our measured value of $+5.2\times10^{-6}$ eV/bar. Goroff and Kleinman,[38] in an earlier and somewhat less refined pseudopotential calculation of deformation potentials in Si, had made the second of these two points and had also questioned the E_0' identification of this peak on this basis. Herman reinterprets the break seen by Tauc and Abraham at $\mathrm{Ge}_{0.2}\mathrm{Si}_{0.8}$ in terms of the crossover of $\Gamma_{2'}{}^{c}$ and $\Gamma_{15}{}^{c}$, and he suggests that the piezoreflectivity data of Gerhardt might require a complex analysis for its explanation.

Although our experimental pressure coefficient for the Si 3.4-eV peak, coupled with theoretical estimates[8,38] for dE_0'/dP, furnishes evidence that the E_0' assignment is incorrect, the pressure data does not provide a clear basis for identifying what the correct assignment is. The calculations of both Herman *et al.*[8] and Kane[26] indicate that an extended volume of the Brillouin zone is responsible for this peak, and both calculations include regions near the Λ axes. This suggests that there may not be any sharp distinction between this peak and the E_1 peaks discussed in the previous section. The coefficient for the Si peak is somewhat smaller than those observed for the E_1 peaks discussed earlier, but it is close to the theoretical estimate of Herman *et al.* for dE_1/dP in Si, so that the net implication is inconclusive. An E_1 assignment for this peak is thus neither contradicted nor established by these results; only a weak statement, that such an assignment is not inconsistent with the pressure data, may be made.

The peak at 3.7 eV in GaP, previously assigned as E_0', has recently been reinterpreted as E_1 on the basis of GaAs-GaP–alloy data[39] and pseudopotential band calculations.[40] The earlier E_0' interpretation was based, in part, on the similarity between this peak and the supposed Si E_0' peak with respect to dependence upon temperature[13] and pressure.[6] As discussed above, a new interpretation now seems to be required for the Si peak, reopening the possibility of a similar assignment for the two peaks. If both peaks are, essentially, E_1

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[35] U. Gerhardt, Phys. Status Solidi **11**, 801 (1965); Phys. Rev. Letters **15**, 401 (1965).

[36] D. Brust, Phys. Rev. **139**, A489 (1965).

[37] R. Braunstein, A. R. Moore, and F. Herman, Phys. Rev. **109**, 695 (1958).

[38] I. Goroff and L. Kleinman, Phys. Rev. **132**, 1080 (1963).

[39] J. C. Woolley, A. G. Thompson, and M. Rubenstein, Phys. Rev. Letters **15**, 670 (1965); T. K. Bergstresser, M. L. Cohen, and E. W. Williams, *ibid.* **15**, 662 (1965); A. G. Thompson, M. Cardona, K. L. Shaklee, and J. C. Woolley, Phys. Rev. **146**, 601 (1966).

[40] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

TABLE II. Pressure coefficients of several energy gaps in group IV and group III-V semiconductors.

Energy gap	Transition		Pressure coefficients in 10^{-6} eV/bar						
	Group IV element	Group III-V compound	Ge	Si	GaP	GaSb	InAs	InSb	Others
E_0	$\Gamma_{25'}{}^{v} \rightarrow \Gamma_{2'}{}^{c}$	$\Gamma_{15}{}^{v} \rightarrow \Gamma_{1}{}^{c}$	+13[b]		+11[c]	+14.5[b,e]	+10[d]	+15[b]	GaAs, +11.5[f]; InP, +8.5[d]
E_1	$\Lambda_{3}{}^{v} \rightarrow \Lambda_{1}{}^{c}$	$\Lambda_{3}{}^{v} \rightarrow \Lambda_{1}{}^{c}$	+7.5[a]	+5[a]	+6[a,c]	+7.5[a]	+7[a]	+8.5[a]	
E_2	$X_{4}{}^{v} \rightarrow X_{1}{}^{c}$	$X_{5}{}^{v} \rightarrow X_{1}{}^{c}$	+5.5[a]	+3[a]		+6[a]		+6[a]	
$E_{\Gamma X}$	$\Gamma_{25'}{}^{v} \rightarrow \Delta_{1}{}^{c}$	$\Gamma_{15}{}^{v} \rightarrow X_{1}{}^{c}$	−1.5[b]	−1.5[b]	−1[c]				AlSb, −1.5[b]
$E_{\Gamma L}$	$\Gamma_{25'}{}^{v} \rightarrow L_{1}{}^{c}$	$\Gamma_{15}{}^{v} \rightarrow L_{1}{}^{c}$	+5[b]			+5[b]			Sn, +5[g]

[a] This work.
[b] See Ref. 3, Table I.
[c] See Ref. 6.
[d] See Ref. 29.
[e] T. Deutsch and B. Kosicki, Bull. Am. Phys. Soc. 9, 60 (1964); B. Kosicki and W. Paul (to be published).
[f] M. DeMeis, Technical Report HP-15, Gordon McKay Laboratory of Applied Science, Harvard University, 1966 (unpublished).
[g] S. Groves, Technical Report HP-10, Gordon McKay Laboratory of Applied Science, Harvard University, 1963 (unpublished).

peaks, then this would establish the same set of transitions as being responsible for the first strong peak seen in all of the group IV and III-V semiconductors studied thus far.

A difficulty remaining with the E_1 interpretation of the GaP peak is the small but distinct break seen in the alloy data in following the GaAs 2.9-eV peak (E_1) to the GaP 3.7-eV peak,[39] which is not yet accounted for. Also, the temperature and pressure coefficients of the GaP 3.7-eV and Si 3.4-eV peaks are alike and are noticeably smaller than the corresponding coefficients for the established E_1 peaks.[6,13] These are indications of a difference in character between these two peaks and the E_1 peaks. Since the transitions responsible for all of these peaks likely occur over a significant fraction of the zone volume,[8,26] this difference may consist only of a quantitative variation in the detailed shape of this region, rather than any strong qualitative distinction (i.e., different sets of critical points), as has been believed in the past.

C. Inventory of Pressure Coefficients, Rigid and Deformable Bands

In Table II, we have assembled a collection of pressure coefficients of various electronic-energy separations which contains most of the available experimental information for the group of materials we have been considering. (Table II brings up to date an earlier compilation by one of the authors.[3]) The second and third rows of the table list the results for the direct transitions E_1 and E_2 discussed in the preceding sections. (The coefficients of the Si 3.4-eV and GaP 3.7-eV peaks discussed above have been tentatively placed with the E_1 coefficients.) The other rows contain results for three other well-studied transitions, the direct transition E_0 and the indirect transitions $E_{\Gamma X}$ and $E_{\Gamma L}$. E_0 labels the $\Gamma_{25'}{}^{v} \rightarrow \Gamma_{2'}{}^{c}$ (diamond structure) and $\Gamma_{15}{}^{v} \rightarrow \Gamma_{1}{}^{c}$ (zincblende structure) transitions responsible, respectively, for the lowest direct gap in Ge at 0.8 eV and in GaAs at 1.4 eV. E_0 coincides with the forbidden band gap in GaAs, GaSb, InAs, InP, and InSb. $E_{\Gamma X}$ denotes the $\Gamma_{25'}{}^{v} \rightarrow \Delta_{1}{}^{c}$ and $\Gamma_{15}{}^{v} \rightarrow X_{1}{}^{c}$ transitions responsible, respectively, for the indirect band gaps of Si and of GaP,[6] while $E_{\Gamma L}$ denotes the $\Gamma_{25'}{}^{v} \rightarrow L_{1}{}^{c}$ transition responsible for the indirect band gap of Ge. All of these transitions are represented by arrows on the Ge band structure shown in Fig. 1(b).

When the equality of $dE_{\Gamma X}/dP$ for Ge and for Si was first established,[2] it was suggested that corresponding energy separations in closely related materials have similar pressure coefficients,[2,3] i.e., that the effect of pressure on the energy of an electronic transition depends primarily on the type of transition involved, rather than the particular material selected from among the group IV and group III-V family of semiconductors. Later work on E_0 and $E_{\Gamma X}$ in the III-V's tended to strengthen this empirical correlation between pressure-coefficient and transition assignment.[3,4] The information contained in Table II gives a current review of the experimental evidence for this correlation. The entries in the table clearly group themselves by rows, in harmony with the view expressed above. Two sets of values comprising two of the rows of Table II are each clearly distinguishable from all of the other sets. These are the coefficients for E_0 and for $E_{\Gamma X}$, the energy intervals which are, respectively, most and least sensitive to pressure. The situation is much less clear cut for the other three energy gaps of intermediate sensitivity to pressure, for which the sets of coefficients overlap to some extent and are not cleanly separable from each other, but the trend for correlation with transition rather than with material remains discernible.

A natural question to ask is whether or not this systematic behavior extends to the zincblende II-VI compounds which are isoelectronic to, although much more polar than, the III-V's and group IV's. The information available is as yet too fragmentary to make a judgment on this. Thomas,[41] from a uniaxial stress experiment, obtained a pressure coefficient of $+11\times10^{-6}$ eV/bar for E_0 in CdTe, matching closely the values in the top row of Table II. Langer,[42] however, from hydrostatic pressure experiments, obtained a value of

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[41] D. G. Thomas, J. Appl. Phys. 32, 2298 (1961).

[42] D. Langer, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 241.

TABLE III. Comparison of experimental and calculated pressure coefficients.

Energy gap	Exptl. coeff. for Ge	Calculated coefficients in 10^{-6} eV/bar			
		Bassani and Brust[a]; pseudopotential calc. for Ge	Goroff and Kleinman[b]; pseudopotential calc. for Si	Cardona and Pollak[c]; full zone $k\cdot p$ calc. for Ge	Herman, Kortum, Kuglin, and Short[d]; nonrel. self-consistent calc. for Ge
E_0	+13	+20	+9	+13	+13.7
E_1	+7.5	+12	+5	+7	+6.7
E_2	+5.5	+7	+2	+2.3	+3.3
$E_{\Gamma X}$	−1.5	+3	−0.3	−1.6	−1.1
$E_{\Gamma L}$	+5	+11	+4	+4.5	+4.7
E_0'	···	+3	+1	+3.5	+0.9

[a] See Ref. 46.
[b] See Ref. 38.
[c] See Ref. 28. The other coefficients are calculated relative to that for E_0, which is chosen to agree with experiment.
[d] See Ref. 8.

$+8\cdot 10^{-6}$ eV/bar for the same coefficient, as well as a value of $+6\cdot 10^{-6}$ eV/bar for E_0 in ZnTe and in ZnS; all of these coefficients are smaller than those listed for E_0 in Table II. Langer's coefficients for E_1 and $E_1+\Delta_1$ in CdTe and ZnTe are $+6\times10^{-6}$ to $+7\times10^{-6}$ eV/bar, falling within the range we observe for groups IV and III-V.

The Ge coefficients listed in Table II enable us to say something about the relative deformability, under pressure, of the valence and conduction bands of this material. Deformability is used here to denote the degree to which an energy band undergoes distortion or warping under pressure; i.e., it refers to changes in *intraband* energy separations with pressure. First, let us assume that dE_1/dP specifies the shift with pressure of $L_{3'}{}^v \to L_1{}^c$ as well as of $\Lambda_3{}^v \to \Lambda_1{}^c$, which is consistent with the near parallelism of the bands between the critical at Λ and the zone boundary at L.[18] Then the pressure dependences of the energy separations corresponding to the transitions $L_1{}^c \to \Gamma_{2'}{}^c$, $X_1{}^c \to \Gamma_{2'}{}^c$, $L_{3'}{}^v \to \Gamma_{25'}{}^v$, and $X_4{}^v \to \Gamma_{25'}{}^v$, are given by the coefficients of $E_0-E_{\Gamma L}$, $E_0-E_{\Gamma X}$, $E_1-E_{\Gamma L}$, and $E_2-E_{\Gamma X}$, respectively. Denoting these four energy separations by $E_{\Gamma L}{}^c$, $E_{\Gamma X}{}^c$, $E_{\Gamma L}{}^v$, $E_{\Gamma X}{}^v$, the corresponding coefficients (in units of 10^{-6} eV/bar) are as follows:

$$dE_{\Gamma L}{}^c/dP=+8\,,\qquad dE_{\Gamma X}{}^c/dP=+14.5;$$
$$dE_{\Gamma L}{}^v/dP=+2.5\,,\quad dE_{\Gamma X}{}^v/dP=+7\,.$$

These results indicate that the conduction band is two or three times as sensitive to pressure as the valence band. This relative rigidity of the valence band is consistent with the observation that this band is less variable from material to material than the conduction band. However, these intraband coefficients demonstrate the danger in employing the concept of an absolutely rigid valence band, since the quantitative difference between the two bands is not very great.

D. Comparison with Calculations: Implications Concerning E_2

We will now compare the data for germanium, which makes up the most complete column shown in Table II, to several theoretical treatments of pressure effects. A summary of the comparisons discussed in this section is shown in Table III. Relatively few calculations of the dependence of band structure on lattice constant have been attempted, which is not surprising since only recently have the band calculations begun to converge upon the experimental picture of the zero-pressure band structure itself.

The earliest theoretical clues to the observed behavior were provided by the core-shift analysis introduced by Herman and Skillman[43] to test the relative reliability of calculated energy levels for Ge. They computed the sensitivity of several conduction- and valence-band eigenvalues to a rigid-energy translation of the ladder of core eigenvalues. Since a connection exists between such core shift trajectories and variations with lattice constant,[44] we might expect to find a similarity between the relative sensitivity of various energy separations to core shift and the relative magnitudes of pressure coefficients. A rough resemblance does indeed show up in that E_0 is very sensitive to core shift and $E_{\Gamma X}$ very insensitive,[43,45] but any more detailed comparison to the pressure coefficients yields only fair correlation.

Later, calculations based on the pseudopotential approach were reported for Ge by Bassani and Brust,[46] and for Si by Goroff and Kleinman[38]; their results are shown in Table III. Although the magnitudes of these theoretical values differ from the experimental ones by roughly a factor of 1.5 (Bassani and Brust's coefficients are too high, Goroff and Kleinman's are too low), relative values of coefficients within each set are in fair over-all agreement with experiment.

Most recently, pressure coefficients for Ge have been calculated by Cardona and Pollak[28] by means of a full-zone $\mathbf{k}\cdot\mathbf{p}$ method, and by Herman *et al.*[8] by means

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[43] F. Herman and S. Skillman, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovak Academy of Sciences, Prague, 1961), p. 20.

[44] W. Paul and H. Brooks, Progr. Semicond. **7**, 145; R. Zallen, Technical Report No. HP-12, Gordon McKay Laboratory of Applied Science, Harvard University, 1965 (unpublished), pp. 120, 121.

[45] J. C. Phillips, Phys. Rev. **125**, 1931 (1962); Ref. 29, Table 4–2.

[46] F. Bassani and D. Brust, Phys. Rev. **131**, 1524 (1963).

of a careful nonrelativistic self-consistent calculation. (In the former calculation, the pressure coefficient for E_0 is chosen to agree with experiment, and the other coefficients are then determined; the latter calculation differs from all of the others mentioned in that it relies to a much lesser extent upon adjustable parameters fitted to experiment, and is more nearly a "first-principles" calculation.) The results of these two calculations, shown in the last two columns of Table III, both agree very well with four of the five experimental values. The lone exception is E_2, the $X_4{}^v \rightarrow X_1{}^c$ energy separation which has been associated with the dominant reflectivity peak. The calculated coefficients for E_2 are significantly smaller than the coefficient measured by us for the large peak. Herman,[8] who finds a similar discrepancy for Si as well as for Ge, cites these results as evidence in support of a view recently arrived at by Kane,[26] in a treatment of the Si band structure, that the main peak (for both materials) comes about as a result of contributions from an extended portion of the zone which includes, but only as a relatively minor contribution, the region near X. A point worth noting here is that, for both Ge and Si, Herman's calculated coefficient[47] for a point along the [110], or Σ, axis, two-thirds of the way out to the zone boundary, is quite close to the measured coefficient of the main peak. Since this point lies right in the middle of the region which Kane associates with the main peak in Si,[48] the implication is strong that transitions near this point are among those which are most representative of the dominant peak.

5. SUMMARY

We have measured and analyzed the effect of hydrostatic pressures to 10 kbar in shifting the energy of peaks in the visible and ultraviolet reflectivity spectra of several group IV and group III-V semiconductors. The results, which give the pressure coefficients of energy separations corresponding to direct interband transitions, are shown in Figs. 3 and 4 and in Table I. All of the interband energy gaps studied were observed to increase with pressure. No appreciable change with pressure, within the experimental accuracy of $\pm 1\times 10^{-6}$ eV/bar, was exhibited by the spin-orbit splitting of the $\Lambda_3{}^v$ valence band.

An up-to-date summary of experimental pressure coefficients for energy separations prominent in the band structures of these materials is given in Table II. The applicability of a previously noted correlation between transition assignment and pressure coefficient is extended and modified by the new data in Table II. The sensitivity to pressure of several intraband energy gaps can be estimated for Ge, with the conclusion being that, for this material, the conduction band is only two or three times as deformable, under pressure, as the valence band.

The measured pressure coefficients, when compared with the results of several recent theoretical calculations, reveal substantial agreement, with the following important exceptions: the calculated coefficients for the $X_4{}^v \rightarrow X_1{}^c$ energy separation in Ge and Si and the $\Gamma_{25'}{}^v \rightarrow \Gamma_{15}{}^c$ (or nearby $\Delta_5{}^v \rightarrow \Delta_1{}^c$) energy separation in Si are much lower than the measured coefficients for, respectively, the dominant E_2 peaks in Ge and Si and the 3.4-eV peak in Si. The discrepancies show that these peaks are not dominated by contributions from the aforementioned transitions.

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[47] Reference 8, Table IV, rows 8 and 9.

[48] Reference 26, Fig. 3(a).