

all of the divergent terms, which we have not succeeded in doing. However, from (16) and (20) we see that the change of S_z due to the s - d interaction is of the order of unity, i.e., independent of J . Our conjecture on the ground-state wave function then is the following: We take $S = \frac{1}{2}$ as the simplest case. Our ground states are represented by that of the Fermi gas multiplied by the up- or down-spin state of the localized spin. The above result indicates that because of the s - d interaction, the state with the opposite spin direction is mixed by an

amount of order unity. Since the exchange interaction conserves the total spin, the spin which was initially carried by the localized spin is now taken over by the conduction electrons. We may quite naturally expect that the twofold degeneracy of our ground state comes from the two directions of the spin carried by the conduction electrons and thus is trivial. This argument reconciles the apparent spin degeneracy of our ground state with the singlet spin state which was assumed in the previous variational approach.^{4,5}

Form Factors and Ultraviolet Spectra of Semiconductors at High Pressure*

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Using the observed pressure dependence of a small set of band edges in Ge and Si, the pressure dependence of the pseudopotential form factors is deduced. Using these pressure-dependent form factors, the energy band structure and ultraviolet spectra are computed as a function of applied pressure. The results appear to give very reasonable agreement when compared with the observed pressure dependence of the reflectivity.

I. INTRODUCTION

BAND-structure calculations in semiconductors at atmospheric pressure have progressed enormously in the last few years. In the case of the group-IV elements (particularly Ge and Si) we can calculate not only the details of the band edges, but also properties depending on the band structure far from the energy gap such as the principal features of ultraviolet reflectivity spectra^{1,2} and photoelectric emission yield and distribution curves.³⁻⁵ Pseudopotential band structures are now also available for a number of partially ionic compounds,⁶ and will presumably also lead to a similar interpretation of ultraviolet data.⁷

Application of large hydrostatic pressures with a consequent decrease in the crystal-lattice dimension results in observable band-structure changes in semiconductors. The experimental situation is described at

length in a review article by Paul and Warschauer.⁸ In germanium, Paul and Brooks⁹ found by analyzing their high-pressure resistivity and electron-mobility data that the fundamental gap increases with a coefficient of 5×10^{-6} eV kg⁻¹ cm².¹⁰ This is the pressure coefficient, then, of the L_1 conduction-band minimum relative to the top of the valance band ($\Gamma_{25'}$). In silicon, on the other hand, the resistivity data showed that the conduction-band minima (Δ_1) move down under pressure. The coefficient was deduced to be¹¹ -1.5×10^{-6} eV kg⁻¹ cm², and was reasonably well confirmed by high-pressure studies of the indirect absorption edge.^{12,13} The direct optical gap in Ge ($\Gamma_{25'} \rightarrow \Gamma_{2'}$) which is nearly degenerate with the indirect gap was observed to shift under pressure at the rate of 12 eV kg⁻¹ cm².¹³⁻¹⁵ The Δ_1 conduction-band edge in Ge lies ~ 0.2 eV above the absolute minima. When pressure is applied to Ge, Δ_1 approaches L_1 and eventually becomes the absolute

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¹ D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 94 (1962).

² D. Brust, Phys. Rev. **134**, A1337 (1964).

³ D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters **9**, 389 (1962).

⁴ D. Brust, Phys. Rev. **139**, A489 (1965).

⁵ E. O. Kane, Phys. Rev. **146**, 558 (1966); in Proceedings of the International Conference on the Physics of Semiconductors, Kyoto, Japan, 1966 (unpublished).

⁶ M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

⁷ T. K. Bergstresser, M. L. Cohen, and D. Brust (to be published).

⁸ W. Paul and D. M. Warschauer, *Solids Under Pressure*, (McGraw-Hill Book Company, Inc., New York, 1963), p. 179.

⁹ W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954).

¹⁰ We shall use kg/cm² as the unit of pressure throughout this paper. To within about 4% this is equal to the other standard pressure units, i.e., the bar and the atmosphere.

¹¹ W. Paul and G. L. Pearson, Phys. Rev. **98**, 1755 (1955).

¹² W. Paul and D. M. Warschauer, J. Phys. Chem. Solids **5**, 102 (1958).

¹³ L. J. Neuringer, Phys. Rev. **113**, 1495 (1959).

¹⁴ H. Y. Fan, M. L. Shepherd, and W. G. Spitzer, *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), p. 184.

¹⁵ M. Cardona and W. Paul, J. Phys. Chem. Solids **17**, 138 (1960).

minimum. Slykhouse and Drickamer¹⁶ found in accordance with these observations that the pressure coefficient of the optical gap in Ge changes sign near 50 000 kg cm⁻². These data as well as anomalous electron-mobility data at high pressures show that the Δ_1 minima move down in Ge at a rate nearly equal to the value found in Si.

One notices that the above measurements all give values for absolute (M_0) conduction-band edges, and one can be quite confident that the interpretations in terms of shifts of definite states relative to the valence band are well established. In order to examine the effects of pressure on the band structure at points other than M_0 edges, Zallen and Paul^{17,18} have measured the movement of the reflectance peaks under hydrostatic conditions. Since these peaks are known to be due to saddle-point edges in the joint interband density of states,² such measurements can be extremely useful in indicating the behavior of the energy bands as a function of pressure over large energy ranges. These studies in common with the band-edge studies indicate that the pressure coefficients of a given level tend to be nearly equal for the family of Group-IV and -III-V semiconductors.

On the theoretical side, considerably less work has been done on the calculation of deformation potentials than on the energy bands at atmospheric pressure. Goroff and Kleinman¹⁹ used an orthogonalized-plane-wave (OPW) technique to derive pressure coefficients for Si. Bassani and Brust,²⁰ on the other hand, used an analytic fit to the pseudopotential formalism in an attempt at a similar calculation in Ge. Both calculations gave correct trends but were not entirely satisfactory from a quantitative viewpoint. More recently, Herman,²¹ using a full OPW technique carried to a point of high self-consistency, calculated the deformation potentials for both Ge and Si. The calculations are limited to a few symmetry points and lines. They can therefore be compared only with the M_0 band-edge data. At these points the agreement between theory and experiment appears satisfactory.

The aim of the present paper is somewhat exploratory. We shall attempt to construct the pressure dependence of the pseudopotential parameters in a manner analogous to the procedure already employed to calculate the atmospheric band structure of Ge and Si. This can be compared with simple theoretical models which predict the lattice-constant dependence of the pseudopotential. Having settled on an appropriate choice for $dV_P(|K|)/dP$ we will then calculate the

deformation of the entire band structure as a function of lattice constant. In order to test the new band structures we will calculate ultraviolet spectra and compare them with experiment. We shall see that although we make no attempt to fit the pressure coefficients of the reflectivity peaks in our empirical adjustment, reasonable agreement with the optical data is achieved throughout. In particular, we shall demonstrate that for complicated saddle-point edges (M_1 , M_2 type), in many cases, reflectivity peak pressure coefficients can *not* be directly correlated with the deformation potential of a single energy gap. Attempts to do so have led to considerable confusion in the literature. We find instead that one must take account of broadening effects to get meaningful results.

II. THE PSEUDOPOTENTIAL AT HIGH PRESSURES

A. Choosing a Pseudopotential

The use of pseudopotentials in semiconductors has been rather thoroughly discussed in the literature.^{2,6} The general theory of pseudopotentials with emphasis on metals is the topic of a recent book.²² We will here adopt the method which has already proved successful in Ge and Si at atmospheric pressure.^{2,4} Briefly we use a local pseudopotential expanded as

$$V_P = \sum_J V_P(K_J) \exp[(2\pi i/a)K_J \cdot r], \quad (1)$$

where K_J are nondimensional reciprocal lattice vectors and a is the lattice constant. We retain only the lowest three *independent* Fourier coefficients permitted by crystal symmetry, i.e., $V(3)$, $V(8)$, and $V(11)$. The neglect of higher Fourier coefficients would seem reasonable on the grounds that the pseudopotential is reasonably smooth even into the core regions where the strong repulsive and attractive terms nearly cancel. Kane⁶ has given strong support to the three-parameter model by studying the effect of higher Fourier coefficients on the band structure. He concludes that the higher Fourier coefficients are *not* linearly independent of the first three in terms of their influence on the band structure. Herman²¹ has reached the same conclusion. The effect of higher terms in the series is simulated by slightly readjusting the lower coefficients.

In order to get an appropriate pseudopotential for the compressed crystals we follow an empirical procedure. As discussed in the introductory section, pressure coefficients for $\Gamma_{25'} \rightarrow \Gamma_2$ and $\Gamma_{25'} \rightarrow L_1$ are well established experimentally for Ge as is the $\Gamma_{25'} \rightarrow X_1$ shift in Si. In the following calculation we will fit our pressure-dependent pseudopotential to the observed values of these coefficients. We note that the $\Gamma_{25'} \rightarrow \Gamma_2$ pressure shift is quite similar over the whole family of

¹⁶ T. E. Slykhouse and H. G. Drickamer, J. Phys. Chem. Solids **7**, 210 (1958).

¹⁷ R. Zallen, Gordon McKay Laboratory of Applied Science, Harvard University, Technical Report HP-12, August 1964 (unpublished).

¹⁸ M. I. Nathan, W. Paul, and H. Brooks, Phys. Rev. **124**, 391 (1961).

¹⁹ I. Goroff and L. Kleinman, Phys. Rev. **132**, 1080 (1963).

²⁰ F. Bassani and D. Brust, Phys. Rev. **131**, 1524 (1963).

²¹ F. Herman (to be published).

²² W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

Group-IV and -III-V compounds.²³ In the following work we have chosen to use a shift for this edge in silicon which is characteristic of the family of zinc-blende semiconductors, although we admit that we introduce some uncertainty into the calculation at this point. That gives us two out of the three conditions necessary to establish a unique set of coefficients to characterize the pressure dependence of V_P . In order to complete the set we will use the shift of $\Gamma_{25'} \rightarrow \Gamma_{15}$ as computed by Herman.²¹ We expect these values to be reasonably close to experiment, since Herman's self-consistent OPW calculations for atmospheric pressures lead to energy gaps which agree with experiment within $\sim 20\%$ where comparison is possible. Furthermore, his pressure shifts agree with the three experimental edges in Ge and Si within $\sim 10\%$. We then have a tentative set of parameters to begin our calculations. We do not expect our present pseudopotential to be the optimum choice. In order to examine its validity for the present study we subject it to three *critical* tests. (i) We require that our full-zone calculations give an account of the observed shifts with pressure of the ultraviolet peaks. This test will serve to assure us that our deformed band structure is a good approximation to the physical situation. (ii) As a weaker condition we require qualitative agreement with Herman's results at symmetry points. We only require that the fit be reasonable since we have no way of assessing the absolute error in Herman's calculations. (iii) We shall require that the pseudopotential deform under pressure in a way consistent with that indicated by general considerations.

B. The Pressure-Dependent Pseudopotential

Using the three pressure coefficients as discussed above we evaluated $dV_P(|K|)/dP$ in Ge and Si, and used the values of $V_P(|K|)_{P=1 \text{ atm}}$ as determined in Ref. 2. The results are shown in Table I. Using the values in Table I we have computed a number of energy gaps and compared our results with the extensive OPW calculations in Table II. It is seen that the present results and the values as deduced by Herman are in surprisingly close agreement.

We may attempt to get a qualitative idea of the expected pressure dependence of the pseudopotential. To do so we can treat the pseudopotential in a rigid-ion

TABLE I. Pressure coefficients of the pseudopotential as deduced and used in this paper.

K	$dV(K)/dP$ in Ry/kg cm ⁻²	
	Ge	Si
$\sqrt{3}$	-0.5×10^{-8}	6.83×10^{-8}
$\sqrt{8}$	13.7×10^{-8}	14.7×10^{-8}
$\sqrt{11}$	13.7×10^{-8}	14.7×10^{-8}

²³ The corresponding edge in the III-V crystals corresponds to $\Gamma_{15} \rightarrow \Gamma_1$ transitions.

TABLE II. The pressure coefficients of several symmetry point gaps.

Gap	$dE_G/dP \times 10^6$, eV/kg cm ⁻²			
	Herman (Ge)	Herman (Si)	Present work (Ge)	Present work (Si)
$\Gamma_{25'} \rightarrow L_1$	4.6	4.1	4.7	4.5
$\Gamma_{25'} \rightarrow X_1$	-1.0	-1.4	-0.9	-1.4
$\Gamma_{25'} \rightarrow \Gamma_{2'}$	13.5	11.9	13.9	13.8
$\Gamma_{25'} \rightarrow \Gamma_{15}$	0.9	0.6	1.0	0.6
$\Gamma_{3'} \rightarrow L_1$	6.6	5.2	6.2	5.8
$L_{3'} \rightarrow L_3$	3.0	1.1	2.1	1.1
$X_4 \rightarrow X_1$	3.3	1.4	2.5	1.8
$W_2 \rightarrow W_1^a$	12.0 ^b	5.7	6.3	5.2
$\Sigma_2 \rightarrow \Sigma_3^a$	5.8	3.1	4.6	2.6

^a W corresponds to the point in the reduced zone (1.0,0.5,0.0); the point chosen on the Σ axis is located at (0.5,0.5,0.0).

^b This is the only sizeable discrepancy between the present work and the OPW work assuming Herman's table does not contain any copy errors.

model. In this case the pseudopotential is simply a linear superposition of atomic potentials. We then can easily derive the following formula:

$$\frac{dV_P(K)}{dP} = C \left[V_P(K) + \frac{K}{3} \frac{dV_P(K)}{dK} \right], \quad (2)$$

where C is the compressibility.

We may then use Eq. (2) to get an approximate set of pressure coefficients. The rigid-ion-model indications appear to give values in rather close agreement with our empirical form factors at large K where we expect the form factors to be characteristic of the bare-ion potential, i.e., for $dV(8)/dK$ and $dV(11)/dK$. As a further check we compare the empirical form factors under pressure with the OPW scattering factors in Fig. 1 as computed by Harrison.²² Again we see the comparison is reasonable.

III. THE PRESSURE DEPENDENCE OF THE ULTRAVIOLET SPECTRA

A. Theory

As in our previous studies¹⁻⁴ of the ultraviolet spectra we shall direct our attention to the calculation of the imaginary part of the frequency-dependent dielectric function, $\epsilon_2(\omega)$. We wish to observe in our calculational framework the shifts of the uv structure as predicted by our form-factor models. To do so we need to use a pressure sufficiently low so that we can be assured that the energy-band deformations are reasonably linear in the applied pressure. We have somewhat arbitrarily taken $P = 61\,000$ kg cm⁻² for both the Ge and Si work. This allows shifts in the uv spectra ~ 0.1 – 0.5 eV. We find that to get good computational resolution a rather small histogram interval is necessary, and this was chosen to be 0.02 eV.

We shall see in the analysis to follow that it is *imperative* to include lifetime-broadening effects in order to correctly evaluate the pressure shifts of the uv

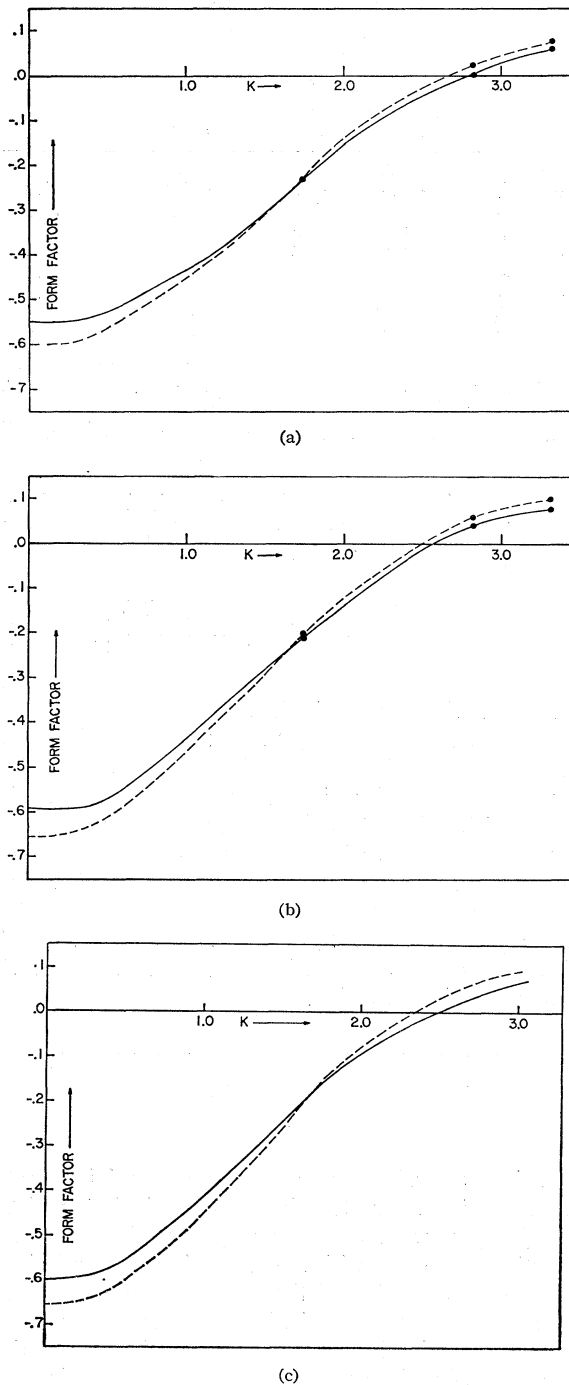


FIG. 1. Pseudopotential form factors in Ry. (a) Ge interpolated, (b) Si interpolated, (c) after Harrison (Ref. 22).

structure. Including Lorentzian broadening, expression (1) of Ref. 2 becomes

$$\epsilon_2(\omega) = \frac{\pi e^2}{m} \sum_{n,s} \sum_k \frac{f_{ns}(k)}{\omega} \frac{\Gamma_{ns}(k)}{[\omega_{ns}(k) - \omega]^2 + [\frac{1}{2}\Gamma_{ns}(k)]^2}, \quad (3)$$

where $\Gamma_{ns}(k)$ is the lifetime broadening, and

$$f_{ns}(k) = \frac{2}{3m} \frac{\hbar |M_{ns}(k)|^2}{\omega_{ns}(k)}, \quad (4)$$

i.e., the interband oscillator strength. For our present purposes we shall treat Γ as a constant. The results of the present discussion are generally not highly sensitive to the precise value of Γ and we are probably well justified in treating Γ as a constant, at least in the vicinity of a given peak. We have chosen $\Gamma = 0.14$ eV which is not far from the value deduced from hot-carrier²⁴ and photoelectric-emission data.²⁵ This choice is probably somewhat high even at room temperatures, and, as we shall see, certain sharp features of the silicon calculation are broadened into the background but can be reclaimed by taking $\Gamma = 0.04$ eV. We may also note that Γ is sufficiently small so that we may take $\omega_{ns}(k) \approx \omega$ over the whole range for which the Lorentzian factor in (3) is appreciable. We then have

$$\epsilon_2(\omega) \approx \frac{2\pi e^2}{3m^2 \omega^2} \sum_{n,s} |M_{ns}|^2 \sum_k \frac{\Gamma}{[\omega_{ns}(k) - \omega]^2 + (\frac{1}{2}\Gamma)^2}. \quad (5)$$

This is the form used in constructing $\epsilon_2(\omega)$. As discussed in Ref. 2 we treat $|M_{ns}(k)|^2$ as a constant. Throughout the work that follows we take $|M_{45}(k)|^2 = 2|M_{i,j}(k)|^2 = \text{constant}$. We also cut off the Lorentzian function for $\omega_{ns}(k) - \omega > \Gamma$.

The histograms have all been constructed by a Monte Carlo procedure as fully described in Ref. 4. According to the discussion of that reference we have used a simple cubic interpolating mesh with a lattice constant equal to 1/20 that of the host reciprocal lattice, and 16 000 Monte Carlo points were used in constructing all the histograms. Bands 3, 4, 5, 6, and 7 were included in the calculation, i.e., the two highest valence and three lowest conduction bands.

In Figs. 2(a)–2(f) we have drawn the behavior of the dielectric function with respect to pressure. In Fig. 2(a) the peak near 2.2 eV (E_1) in Ge is shown at atmospheric pressure and at our choice of high pressure. We have previously found² that the peak is associated with an M_1 critical point (c.p.) in the 4–5 interband density of states located on the Λ axis. Accordingly we have shown the 4–5 contribution to $\epsilon_2(\omega)$ separately from the background of the remaining pairs of bands. The arrows point out that the inclusion of the Lorentzian factor has tended to put the peak at somewhat *higher* energy than that of the corresponding Van Hove singularity. Because of this asymmetric broadening effect, the

²⁴ W. Shockley, in *Proceedings of the International Conference on Semiconductor Physics, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961).

²⁵ Theoretical estimates as well as an account of the experimental situations are to be found in Ref. 5.

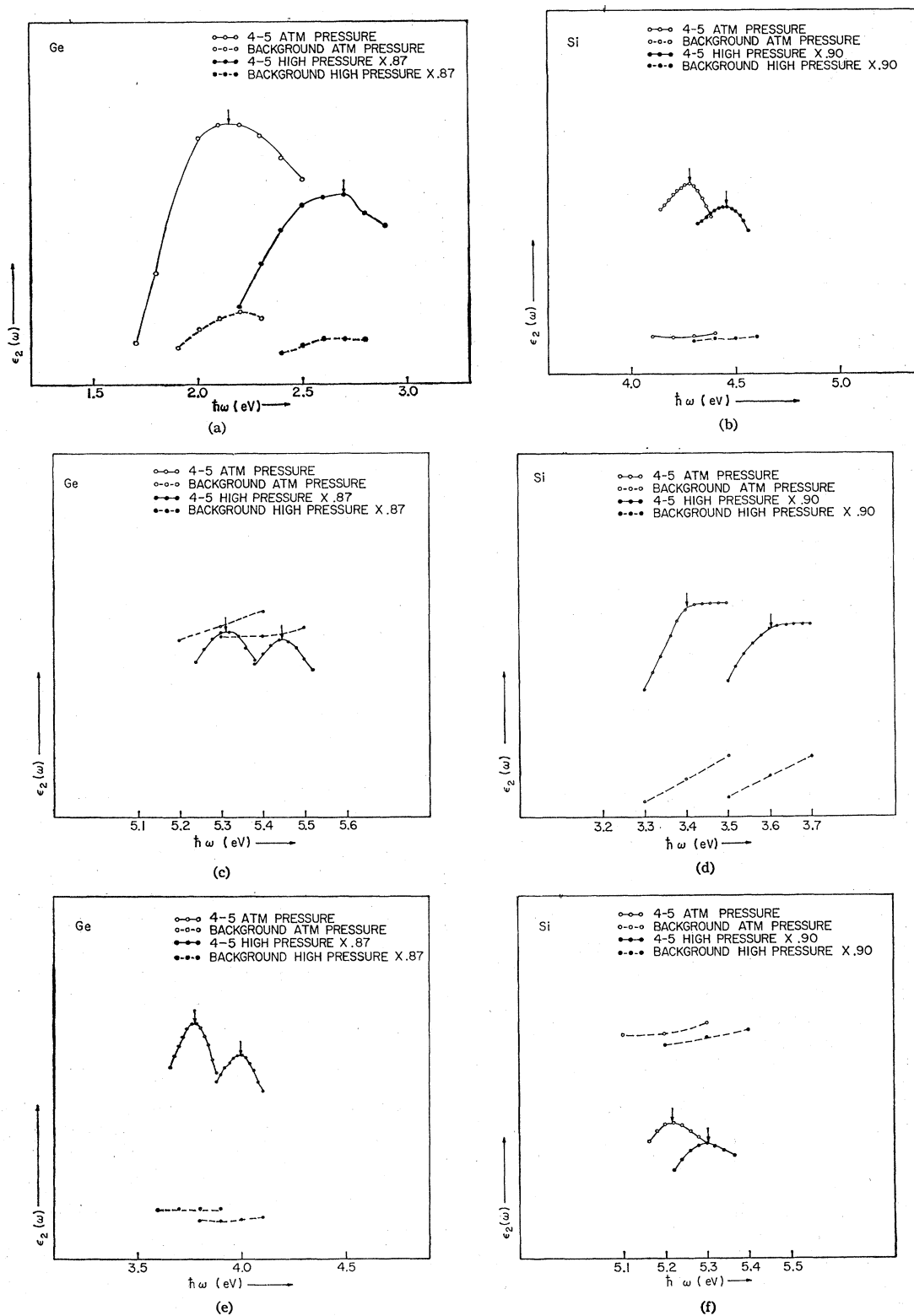


FIG. 2. Pressure dependence of the optical spectra of Ge and Si. $\epsilon_2(\omega)$ is shown in arbitrary units. The scale is chosen in each figure for convenience. The high-pressure case is calculated at $61\,000\text{ kg cm}^{-2}$ for both Ge and Si. The background refers to contributions from all pairs of bands (3,4,5,6,7) exclusive of the 4 \rightarrow 5 transition. For a discussion of line shapes, intensities, oscillator strengths, and pressure coefficients refer to the text. We have separated a normalization factor in the high-pressure case for drafting convenience.

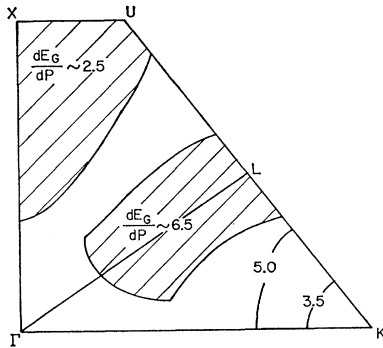


FIG. 3. Sketch of the deformation-potential contours for the $4 \rightarrow 5$ transitions in Ge. The plane chosen is the 110 plane. Shaded areas refer to regions over which the corresponding pressure dependences remain constant. Units are in 10^{-6} eV/kg cm^{-2} .

pressure shift of an M_1 peak will depend both on the pressure coefficient of the c.p. as well as on the effect of stress on the unbroadened line shape. We may think of this effect in terms of the energy contours. Since the interband-energy contours are not closed around an M_1 c.p. (as they are for M_0 c.p.), states far from the c.p. contribute to the line shape of the peak. These states may have substantially different deformation-potential constants. Hence the peak can have a pressure coefficient which differs from that of the critical point itself. In particular we note, however, that the shift of the $\Lambda_3 \rightarrow \Lambda_1$ peak in Ge is rather close to that of the $\Lambda_3 \rightarrow \Lambda_1$ c.p. itself. This is easily understood through examination of Fig. 3. Here we have drawn a few important contours of constant interband-gap deformation potential. We may note that the region around and including the Λ axis has nearly a uniform pressure shift for the 4–5 transitions. Our previous work² has shown that the contours of $E_{45}(k) \approx 2.0$ eV are concentrated in the region. The entire region shifts under pressure in a nearly rigid manner, thus accounting for the observed pressure shift of the optical peak. Finally we note that our peak gets weaker at higher pressure. This is explained by the presence of a factor $1/\omega^2$ in Eq. (5), since the joint density of states maintains a nearly constant strength under pressure. We have taken the momentum matrix element as constant with respect to hydrostatic stress.²⁶

Next we turn to the large peak under 4.3 eV in Ge (E_2). Our previous analysis indicated the origin to be a pair of c.p., one near $X(M_1)$ and the other on the Σ axis (M_2). Kane⁵ has recently made a very careful mapping of the energy contours (in Si) in the 110 plane. He finds, in addition to our previous identifications, additional c.p. nearly degenerate in energy with our previous pair. As we see from examinations of Fig. 2(b) the lifetime broadening has caused all traces of the quasidegenerate c.p. to vanish into one rather well-rounded peak. It is clear immediately that one cannot associate the pressure coefficient of a single c.p. with

²⁶ We take the dimensionless momentum matrix element as constant so that the matrix element in Eq. (5) varies like $1/a^2$. We also note that an additional factor of $1/a^3$ enters into the formula for $\epsilon_2(\omega)$ as a consequence of the decrease in the unit-cell size with compression.

that observed for the peak. We note that the region around X and U has a pressure coefficient smaller than that of the peak. The region around K also makes an important contribution to observed intensity, and the shift must be taken as an appropriate *average* of all contributing states as we have done by use of Eq. (5).

Finally we note that the shift of the $L_3' \rightarrow L_3$ peak is slightly different in the present analysis from that of the $L_3' \rightarrow L_3$ transition. We have not attempted the type of energy-contour analysis used above. Again one must use care before making assignments.

The discussion of Si follows that of Ge and we will not give an extensive discussion. We do note, however, that the narrow peak we previously found⁴ has been broadened into the background. We have found that taking $\Gamma=0.04$ eV brings the peak back into sharp relief, and it shows the same pressure coefficient as the shoulder. Our calculations indicate that the peak rapidly decreases in intensity under pressure. We are not yet certain if this is a peculiarity of our model arising from the extreme sensitivity of this peak to the energy-band details. This point requires further analysis.

B. Comparison of Theory with Experiment

Using the results presented in Fig. 2 we have determined the pressure coefficients of the peaks and edges in the ultraviolet spectra of Ge and Si. The results are given in Table III. We have also shown the experimental¹⁷ results obtained by multiple-reflection methods under pressure. In general the comparison appears quite reasonable. We note that a large (\sim factor 2) difference exists between the experimental shifts of the E_2 peak for Ge and Si. Although we note a similar decrease on going from Ge to Si, it is smaller than experiment.

A number of experiments have also recently measured the piezo-optic effect^{27–31} and the piezo-electro-optic effect³² in semiconductors. These methods, in some cases, have given values for the shifts of critical points associated with the hydrostatic component of uniaxial stress. Here one may hope to separate the different pressure dependence of the c.p. contributing, for example, to the E_2 peak.

IV. GENERAL DISCUSSION

We have used the calculated wave functions and energy gaps to evaluate the change in the transverse effective mass in Si. The principal contributions come from the $\Delta_5^V \rightarrow \Delta_1^C$ band gap. The change appears quite small ($\sim 1\%$) for the chosen pressure.

²⁷ E. Adler and E. Erlbach, Phys. Rev. Letters **16**, 87 (1966).

²⁸ U. Gerhardt, Phys. Rev. Letters **15**, 401 (1965).

²⁹ W. E. Engeler, H. Fritzsche, M. Garfinkel, and J. J. Tieman, Phys. Rev. Letters **14**, 1069 (1965).

³⁰ G. W. Gobeli and E. O. Kane, Phys. Rev. Letters **15**, 142 (1965).

³¹ I. Balslev, Phys. Rev. **143**, 636 (1966).

³² F. H. Pollak, M. Cardona, and K. L. Shaklee, Phys. Rev. Letters **16**, 942 (1966).

TABLE III. Comparison of theoretical and experimental pressure shifts of the principal features in the Ge and Si ultraviolet spectra.

	Position of peak or edge (eV)	Shift of peak in units of 10^{-6} eV/kg cm^{-2}
Ge (theory)	2.15	7.5
	3.8	4.0
	5.3	2.0
Si (theory)	3.4	3.9
	4.3	2.8
	5.2	1.3
Ge (experiment)	2.2	7.5 ± 1.0
	4.3	5.5 ± 1.0^a
	5.6	
Si (experiment)	3.4	5.2 ± 0.5
	4.4	2.9 ± 0.5
	5.4	

^a R. Zallen (private communication).

We have also attempted to make a rough estimate of $d\epsilon_1(0)/dP$, where $\epsilon_1(0)$ is the static (real) dielectric constant. This was evaluated for Ge and Si at atmospheric pressure in Ref. 2 using the well-known formula

$$\epsilon_1(0) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\epsilon_2(\omega)}{\omega} d\omega, \quad (6)$$

as follows from the Kramers-Kronig relations. In the preceding work Eq. (6) was evaluated using only $\epsilon_2^{4 \rightarrow 5}(\omega)$ in the integrand, i.e., the nearest occupied and unoccupied bands. For Ge and Si we got, respectively, 12 and 8 compared with the experimental values of 16 and 12, indicating a reasonably constant contribution from distant bands. This suggests that one estimate the pressure dependence of $\epsilon_1(0)$ by assuming the entire shift arises from the deformation of $\epsilon_2^{4 \rightarrow 5}(\omega)$ under pressure. Using a relatively rough numerical integration procedure we find

$$\frac{d\epsilon_1^{\text{Ge}}(0)}{dP} \approx -34 \times 10^{-6} \text{ kg cm}^{-2}$$

and

$$\frac{d\epsilon_1^{\text{Si}}(0)}{dP} \approx -3.4 \times 10^{-6} \text{ kg cm}^{-2},$$

compared with the experimental result of -22×10^{-6} kg cm^2 and -7×10^{-6} kg cm^{-2} , respectively.⁸ We have

broken the integral (6) into various contributing regions. In particular, nearly the entire decrease of the static dielectric constant in Ge appears to come from a region (< 3.6 eV) which includes the $\Lambda_3 \rightarrow \Lambda_1$ peak. It appears reasonable then to explain the decrease of $\epsilon_1(0)$ with pressure in Ge as due to the increase of the $\Lambda_3 \rightarrow \Lambda_1$ gap. In silicon our value is too small. We may trace these errors to the fact that the pressure coefficient of the 3.4-eV edge is less than observed by a factor of $\sim \frac{1}{4}$. Correcting for this would lead to a value of $\epsilon_1(0)$ in better agreement with experiment.

V. CONCLUDING REMARKS

We have shown that, starting with a reasonably good set of pressure coefficients for three symmetry-point splittings, a very reasonable picture emerges for the optical and ultraviolet spectra of Ge and Si. We emphasize that none of the peaks have been fit by our parametrization procedure. In particular we find the atomic form factors as a function of pressure. The form factors vary in a manner quite similar to what is expected from first-principles considerations. In particular we note that Phillips's³³ arguments concerning the validity of the pseudopotential appear to work surprisingly well even at high pressures. We may also note that spin-orbit splitting has not been included in the present discussion, although in principle one may easily include it.³⁴

Finally we may note that we used three independent coefficients in our adjustment procedure. The calculations indicate that $dV_P(3)/dK$ is rather small compared with the other two. Furthermore the optical energy gaps are considerably less sensitive to changes in $V(3)$ than in $V(8)$ and $V(11)$.² It would, therefore, not be an entirely unreasonable procedure to take $dV_P(3)/dK = 0$ and work with a two-parameter model.

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³³ J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

³⁴ D. Brust and L. Liu, Solid State Commun. **4**, 193 (1966).