we find

$$\mathrm{An}\{e\mathbf{E}'\cdot\nabla_{\mathbf{K}'}A\}=\frac{(e\mathbf{E}')^2}{m}\left\{\frac{dS}{d\epsilon}\left[\frac{2\epsilon\omega}{3}\frac{d}{d\epsilon}\left(\frac{\tau^2}{1+\omega^2\tau^2}\right)P_2^2(\cos\theta)\sin\phi-\frac{4\epsilon}{3}\frac{d}{d\epsilon}\left(\frac{\tau}{1+\omega^2\tau^2}\right)P_2^0(\cos\theta)\right]\right.$$

$$\left.+\frac{d^2S}{d\epsilon^2}\left[\frac{2\epsilon\omega\tau^2}{3(1+\omega^2\tau^2)}P_2^2(\cos\theta)\sin\phi-\frac{4\epsilon\tau}{3(1+\omega^2\tau^2)}P_2^0(\cos\theta)\right]\right\}. \quad \text{(A1)}$$

Comparing this with the other terms in Eq. (4) we find that for $\omega^2\tau^2\ll 1$ the neglect of $\mathrm{An}\{e\mathbf{E}'\cdot\nabla_{\mathbf{K}'}A\}$ is equivalent to neglecting $e\mathbf{E}l/\epsilon$ compared to unity for the cases where phonon equipartition is valid. From Eq. (26) we see that $e\mathbf{E}l/\epsilon\sim(mC_l^2/kT)^{1/2}$, while for the hot Maxwellian distribution, Eq. (9), we find $e\mathbf{E}l/\epsilon\sim e\mathbf{E}l/kT_e$. In both cases the terms are very small compared to unity. When $\omega^2\tau^2\gg 1$ one can neglect the $\mathrm{An}\{e\mathbf{E}'\cdot\nabla_{\mathbf{K}'}A\}$ term for the high-temperature case (equipartition of acoustical phonons) if

$$1\gg\left(\frac{pmC_l^2}{\omega C_2^2[1+pkT/\omega C_2^2]}\right)^{1/2}\sim\frac{(pkT/\omega C_2^2)^{1/2}(mC_l^2/kT)^{1/2}}{(1+pkT/\omega C_2^2)^{1/2}}\sim(mC_l^2/kT)^{1/2}. \quad \text{(A2)}$$

The condition $\omega^2\tau^2\gg 1$ is only realized in high magnetic field in this case, since the average relaxation time decreases because the electrons populate higher energy ranges in the presence of a strong electric field.

If we consider the number of electrons per unit energy range we find that the maximum of this function is displaced towards the higher energies because of the electric field, while the magnetic field displaces the peak towards the thermal equilibrium value. Thus, the electric field "heats" the electrons while the magnetic field "cools" them. Similar results hold for the low-temperature case.

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PHYSICAL REVIEW VOLUME 131, NUMBER 4 15 AUGUST 1963

# Effect of Alloying and Pressure on the Band Structure of Germanium and Silicon*

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(Received 18 January 1963; revised manuscript received 22 April 1963)

The pseudopotential method has been used to compute the band structure of germanium-silicon alloys and the band structure of germanium under high pressure. In the former case the parameters were chosen from a linear interpolation between the parameters used previously for pure germanium and pure silicon, while in the latter case a simplified expression for the pseudopotential parameters based on the orthogonalized plane wave method was used to estimate their variation with lattice constant. The results are in reasonable agreement with experimental observations on the variation with pressure and alloying of the principal band edges. The calculations also indicate that the first absorption peak due to direct transitions should have a much larger pressure coefficient in Ge than in Si.

## I. INTRODUCTION

A VERY useful way of obtaining detailed information on the band structure of simple semiconductors has been to study the change produced in their physical properties by alloying one semiconductor with another. Johnson and Christian[1] studied the change of the energy gap of Ge-Si alloys as a function of silicon concentration. The energy gap increases rapidly up to ~15% Si and from there on the increase is slow until the value in pure silicon is reached. Herman[2] speculated that this result is due to the role of two different minima in the conduction band: up to ~15% Si the $L_1$ state at $\mathbf{k}=(2\pi/a)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is the absolute minimum of the conduction band and when more silicon is added the absolute minimum is shifted to a point along the [100] direction near the state $X_1$ at $\mathbf{k}=(2\pi/a)(1,0,0)$ which is practically insensitive to addition of silicon. This interpretation was confirmed most strikingly by Glicksman,[3] who was able to determine the symmetry of the conduction minima for varying alloy concentration from the properties of the magnetoresistance

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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tensor. A very detailed analysis of the optical absorption edges was carried out by Braunstein, Moore, and Herman[4] and added further support to Herman's interpretation, it also gave information on the change with composition of the direct energy gap $\Gamma_{2'}-\Gamma_{25'}$. A similar suggestion was made by Paul and Brooks[5] to explain their experiments on the effect of high pressure on pure germanium. The conduction minimum $L_1$ in germanium moves upward under the effect of pressure with respect to the top of the valence band with a pressure coefficient $5\times10^{-6}$ eV kg$^{-1}$ cm$^2$, while the conduction minimum at $\Delta_1$ remains nearly constant with respect to the top of the valence band. Further information about the behavior under pressure and alloying of another conduction minimum $\Gamma_{2'}$ has also been obtained.[4,6] From the measured absorption of very thin germanium films under pressure Cardona and Paul[7] obtain for the change in the transition energy $\Gamma_{2'}-\Gamma_{25'}$ the coefficient $12\times10^{-6}$ eV kg$^{-1}$ cm$^2$, in good agreement with other estimates of the pressure effect on the $\Gamma_{2'}$ conduction band edge.[6] More recently, Tauc and Abraham[8] have measured the position of the reflectivity peaks in Ge-Si alloys as a function of the concentration of Si. Since the peaks are due to interband transitions at band edges, their experiments have also been a useful tool in interpreting such transitions in pure Ge and in pure Si.[9] In general, the behavior of the band edges of Ge under pressure is qualitatively the same as their behavior under alloying with silicon and this is probably related to the fact that both pressure and alloying decrease the lattice parameter from its initial value. As pointed out by Paul,[6] however, the change of the lattice constant by alloying produces an effect on the sensitive band edges about three times larger than the same change of the lattice constant by pressure so that it appears that there is a characteristic effect due to alloying besides the decrease in the lattice constant.

In the present paper we make use of the semiempirical pseudopotential method[10] to compute the change in the band structure of Ge due to alloying and pressure. In Sec. II we briefly describe how the parameters of the pseudopotential method can be made to depend on pressure and alloying. In Sec. III we present the results of the calculations of the band structure obtained from appropriate modification of the parameters and compare them with experiments.

## II. PARAMETERS OF THE PSEUDOPOTENTIAL METHOD

The pseudopotential method has been recently used in a semiempirical way to compute the band structure and the joint density states of Ge and Si throughout the Brillouin zone.[11,12] It amounts essentially to an approximation to the orthogonalized plane wave (OPW) method in which the effective Hamiltonian is simplified to a form which is local and eigenvalue-independent. Consequently, the electron eigenvalues are obtained as solutions of secular equations whose matrix elements depend solely on the kinetic terms and on the Fourier coefficients of an effective potential $V_{\text{eff}}(|\mathbf{h}|)$, where $\mathbf{h}$ is a reciprocal lattice vector. These Fourier coefficients consist of the sum of two terms, one originating from the crystal potential and the other from a repulsive-like potential due to the core states of the crystal. The theoretical basis for this approximation and the simplification involved have been discussed in a number of papers.[10] It has been found that for Si and Ge the simplifications are too drastic to be used in an *ab initio* calculation, but they can be accepted when the $V_{\text{eff}}(|\mathbf{h}|)$ are treated as disposable parameters. By retaining as different from 0 three parameters $V_{\text{eff}}(3)$, $V_{\text{eff}}(8)$, and $V_{\text{eff}}(11)$, where the integer numbers indicate the quantity $(a^2/4\pi^2)|\mathbf{h}|^2$, it has been possible to reproduce for both Ge and Si an energy band structure which is very similar to that obtained from detailed OPW calculations. We do not understand clearly the limitations of the pseudopotential approximation, which has also been applied to metals to give a nearly free electron model. Ham[13] has shown that in the case of the alkali metals a simple application of the pseudopotential method such as we have used in this paper would give rise to serious inconsistencies with the results of accurate calculations at symmetry points. We have not investigated the problem accurately enough to be able to tell why the same approximation seems to apply in semiconductors and not in the alkali metals. In a true sense it does not apply in either case because the effective Hamiltonian is nonlocal, but it seems reasonable that a smaller error is made by using a local effective Hamiltonian when there are four valence electrons per atom and the core is smaller than when there is only one valence electron and a much larger contribution from the core. We follow the view that the pseudopotential approximation can be adopted only when it does not give rise to serious contradiction with experiments or with very accurate calculations. The parameters which have been used to obtain the band struction of Ge are $V_{\text{eff}}(3)=-0.230$ Ry, $V_{\text{eff}}(8)=0$ Ry, $V_{\text{eff}}(11)=+0.06$ Ry, and $V_{\text{eff}}(|\mathbf{h}|^2)=0$ for $|\mathbf{h}|^2\gg11$ in units of $(2\pi/a)^2$. The parameters which we

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use to obtain the band structure of Si are $V_{\mathrm{eff}}(3) = -0.220$ Ry, $V_{\mathrm{eff}}(8) = +0.04$ Ry, $V_{\mathrm{eff}}(11) = +0.08$ Ry, and $V_{\mathrm{eff}}(|\mathbf{h}|^2) = 0$ for $|\mathbf{h}|^2 \gg 11$ in units of $(2\pi/a)^2$. The pseudopotential parameters for Ge and Si are not very different in spite of the different size of the atoms because the potentials near the nucleus where most of the difference between Ge and Si occurs are practically cancelled by the repulsive potentials originating from the core states and the lattice constants of two substances are only slightly different (5.65 and 5.43Å, respectively).

The pseudopotential method can be used to compute the band structure of Ge-Si alloys provided one interprets the pseudopotential parameters as the Fourier coefficients of an effective potential averaged over all possible atomic configurations of the disordered alloy. Parmenter[14] has shown that this model of the "virtual crystal" obtained from an averaged potential which has the same symmetry as the potential in the perfect lattice is exact to first order of perturbation theory. The validity of the model is supported by a number of experiments such as the temperature dependence of the optical absorption[4] (Braunstein, Moore, and Herman), successful cyclotron resonance experiments on alloys with relatively higher concentration of silicon,[15] and Tauc's experiments on direct transitions.[8] In practice, we obtain the pseudopotential parameters for the alloy by interpolating between the parameters for pure Ge and pure Si as functions of the relative concentration or of the lattice constant. For this purpose the lattice constant and the relative concentration in the alloy can be considered as linearly related to a good approximation.[1]

For the small changes in volume produced by pressure, the calculational framework must remain valid and the only physical quantity which is changed is the lattice parameter. Consequently, the effect of pressure on the band structure of Ge can be estimated in a similar way from the pseudopotential scheme by obtaining a change in the parameters from a change in the lattice constant. This is not a straightforward procedure because we do not have an analytic expression for the pseudopotential parameters. However, we may relate the pseudopotential parameters to the parameters of the OPW method to obtain a reasonable estimate of such a change. The effective potential in the OPW scheme consists of the attractive crystal potential plus a repulsive-like potential due to the orthogonalization to core states. The differences between the Fourier coefficients of the two terms correspond to the pseudopotential parameters. Both terms increase by comparable amounts when the lattice constant decreases so that the difference is only slightly affected. From the general OPW calculations in Ge we have seen[16] that for $\Delta a/a = -0.0265$ the important Fourier coefficients of the crystal potential change by ~5.2%, while the corresponding orthogonality terms change by ~6%; their difference is nearly unchanged in the case of $V_{\mathrm{eff}}(3)$ and it is slightly increased for $|\mathbf{h}|^2 \gg 3$. To reproduce this situation in the pseudopotential scheme with a simpler analytic expression, we take for the atomic-like potential in Ge a Coulomb screened expression $Ae^{-\alpha r}/r$

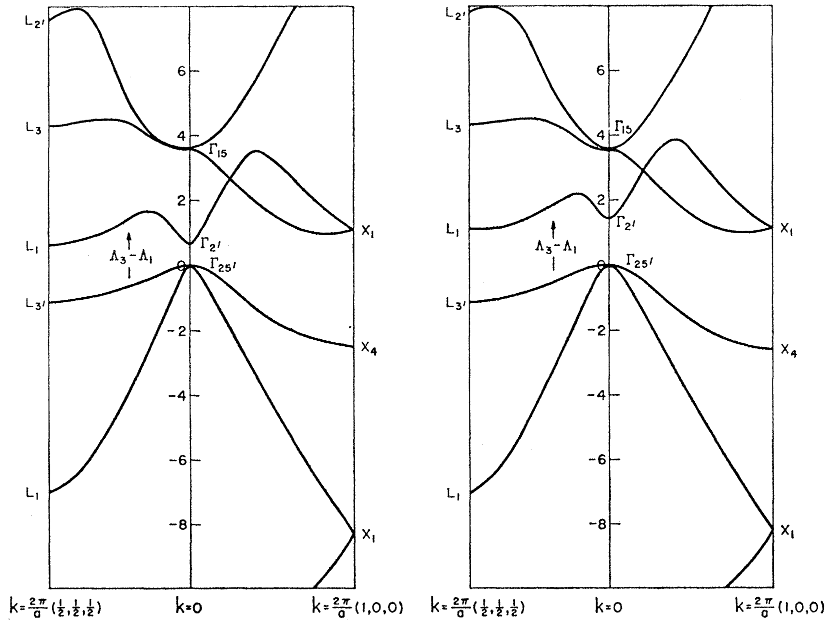

FIG. 1. Energy bands along the direction Δ and Λ for pure germanium (drawing on the left) and for a germanium-silicon alloy with 20% silicon (drawing on the right). For pure germanium the pseudopotential coefficients (in rydbergs) were: $V_{\mathrm{eff}}(3) = -0.230$, $V_{\mathrm{eff}}(11) = 0.060$, and $V_{\mathrm{eff}}(8) = 0.000$ and the lattice constant $a = 5.65$ Å, while for the alloy $V_{\mathrm{eff}}(3) = -0.228$, $V_{\mathrm{eff}}(8) = 0.009$, $V_{\mathrm{eff}}(11) = 0.065$, and $a = 5.60$ Å.

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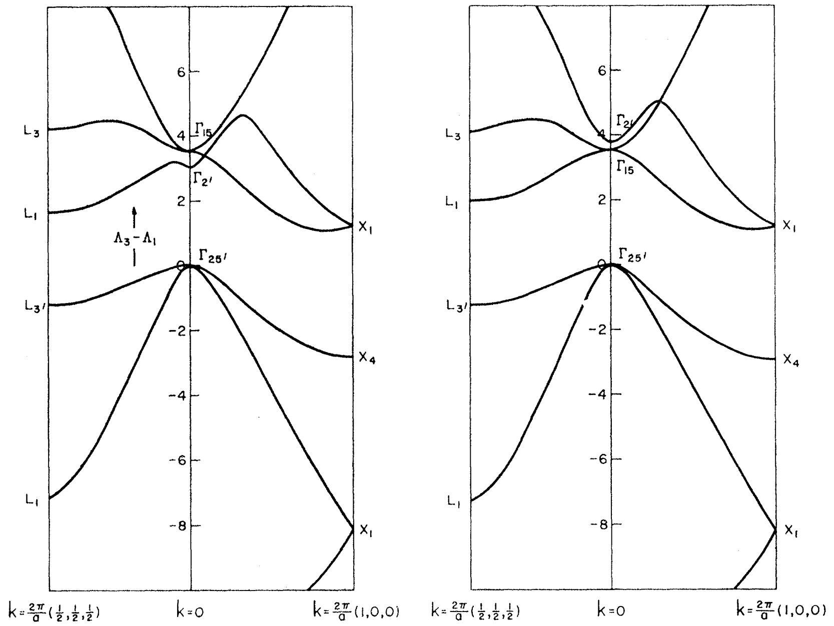

FIG. 2. Energy bands along the directions Δ and Λ for a germanium-silicon alloy (drawing on the left) containing 74% Si and for pure silicon (drawing on the right). For the alloy the pseudopotential coefficients (in rydbergs) were $V_{\rm eff}(3)=-0.223$, $V_{\rm eff}(8)=0.030$, and $V_{\rm eff}(11)=0.075$ and the lattice constant $a=5.49$ Å, while for pure silicon $V_{\rm eff}(3)=-0.220$, $V_{\rm eff}(8)=0.040$, $V_{\rm eff}(11)=0.080$, and $a=5.43$ Å.

and for the repulsive potential only the term originating from orthogonalization to the 3$s$ core state whose radial wave function is indicated by the Slater expression $P_{3s}(r)=Cr^3e^{-\epsilon r}$. We then obtain

$$V_{\rm eff}(|h|)=-\frac{A}{a}\frac{1}{\alpha^2(a^2/4\pi^2)+G^2}+Ea^3\frac{\epsilon^2(a^2/4\pi^2)-G^2}{[\epsilon^2(a^2/4\pi^2)+G^2]^4}, \quad (1)$$

where the dimensionless quantity $G^2=(a^2/4\pi^2)|\mathbf{h}|^2$ can be 3, 8, and 11, $a$ is the lattice constant, and $A$, $\alpha^2$, $E$, $\epsilon^2$ are adjustable parameters which do not depend on the lattice constant. $E$ depends on $C$, $\epsilon$, and on the 3$s$ core eigenvalue and has been used directly in formula (1) as an independent parameter. We obtain results very close to the pseudopotential parameters used to compute the energy bands of Ge by taking $\alpha^2\simeq3$, $\epsilon^2\simeq50$, $A=168.96$, and $E=3.0948\times10^3$; atomic units have been used with the rydberg as the unit of energy. From expression (1) and the above values for the parameters we can follow the variation of $V_{\rm eff}(|\mathbf{h}|)$ as a function of the lattice constant.

The change in pseudopotential parameters obtained from formula (1) or by interpolating between Ge and Si is always very small and is qualitatively similar. In both cases the $V_{\rm eff}(3)$ is nearly unchanged and $V_{\rm eff}(8)$ and $V_{\rm eff}(11)$ increase with decreasing lattice constant. There are differences, however, which can be seen from the parameters listed under Figs. 1, 2, and 3: $V_{\rm eff}(3)$ changes in the opposite direction with alloying than with pressure and $V_{\rm eff}(8)$ and $V_{\rm eff}(11)$ increase less under pressure than under alloying for the same change of lattice parameter. Though formula (1) is the result of a drastic simplification and there may be some uncertainty in the interpolation of the pseudopotential parameters between Ge and Si, such changes in the pseudopotential parameters are probably meaningful for a first understanding of the changes produced in the band structure by alloying and pressure.

### III. RESULTS AND DISCUSSION

The calculation of the band structure of Ge-Si alloys has been performed from the pseudopotential parameters described in the preceding section. In Fig. 1 we have plotted the energy band profiles in the symmetry direction Δ and Λ for pure Ge and for a Ge-Si alloy containing

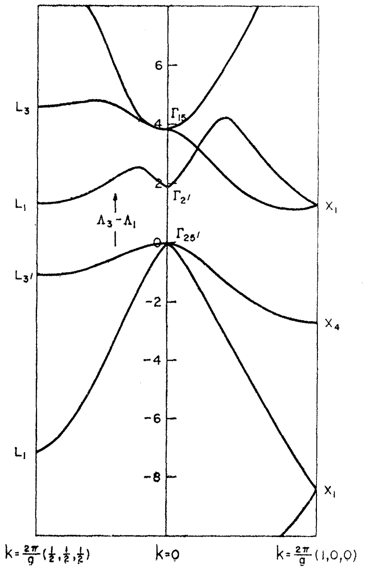

FIG. 3. Energy bands for pure germanium under high pressure. The pseudopotential coefficients (in rydbergs) are $V_{\rm eff}(3)=-0.236$, $V_{\rm eff}(8)=0.012$, and $V_{\rm eff}(11)=0.072$ and the lattice constant $a=5.50$ Å. These parameters correspond to a pressure of ~61 000 kg cm$^{-2}$. Such a high pressure was chosen in order to make the alteration in the energy bands more evident.

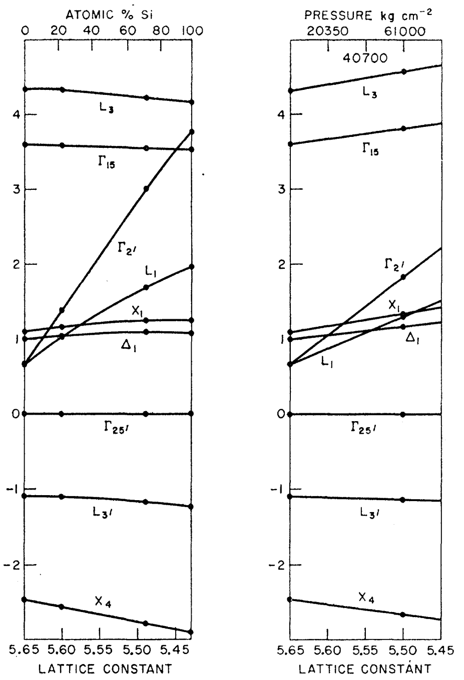

FIG. 4. Variation of major band edges as a function of the silicon concentration in the Ge-Si alloys (drawing on the left) and as a function of pressure in Ge (drawing on the right).

about 20% Si. In Fig. 2 we present the band structure obtained for an alloy with about 75% Si as well as for pure Si. The band structure for pure Ge is the same one computed in Ref. 11, while the band structure of pure Si is slightly different from the one reported in Ref. 12, Fig. 1, because of a slightly different choice of parameters.

By examining the two sets of diagrams jointly we see the following: At the center of the zone the singlet level $\Gamma_{2'}$ moves up rapidly with increasing Si content (all levels are measured with respect to the top of the valence band, i.e., $\Gamma_{25'}$) while the triply degenerate level $\Gamma_{15}$ is nearly insensitive to alloying. At the point $L$ the singlet $L_1$ rises quickly as Si is added, whereas the doubly degenerate levels $L_{3'}$ and $L_3$ are practically unchanged. At the point $X$ the levels are little affected by the alloying as is the relative minimum in the conduction band $\Delta_1$. The energy of the direct transition labeled as $\Lambda_3 \to \Lambda_1$ in Figs. 1 and 2 increases noticeably as the percentage of silicon is enhanced and the location of the transition moves toward the center of the zone. From the diagrams one sees that this transition denotes the point where the valence and the conduction band become parallel.

In Fig. 3 we have plotted the energy bands deduced for the case of Germanium compressed isotropically. As can be seen the effect produced on the bands is very much like that produced by alloying. The alteration in the bands, however, is faster when the lattice constant is reduced by alloying than when reduced by pressure. To illustrate this point we have drawn in Fig. 4 the values of the band edges as a function of lattice constant in both cases of alloying and pressure.

The change in the $\Gamma_{2'}-\Gamma_{25'}$ transition with alloying is in fair agreement with that reported by Braunstein, Moore, and Herman[4] from their optical absorption experiments with up to 12% Si content, though it is larger in our calculation (~0.32 eV as compared to ~0.24 eV at 10% Si). The variation of the indirect gap with alloying has been experimentally studied in great detail. A comparison between our results and the experimental results of Braunstein, Moore, and Herman[4] is presented in Fig. 5 and shows reasonable agreement. In particular, the discontinuity in slope at about 15% Si is reproduced and the interpretation given by Herman[2] is confirmed by the present calculation. Our calculations do not reproduce the quadratic deviation from linearity observed by Braunstein, Moore, and Herman[4] in the indirect energy gap. Such small deviations can be due to pecularities in the phonon spectrum of the alloy as discussed by Braunstein, Moore, and Herman[4] and also to second-order corrections to the "virtual crystal model," as pointed out by Cardona[17] for the case of mixed cuprous halide crystals.

In Fig. 5 we have also plotted the theoretical variation of the first main optical peak and we compare it with the experimental results of Tauc and Abraham. The agreement is satisfactory and we find a discontinuity in slope at about 87% close to the experimental value of 79%. As discussed earlier,[11] the peak studied by Tauc and Abraham which occurs at 2.1 eV in pure Ge arises in that substance as a result of a critical point associated with a $\Lambda_3-\Lambda_1$ critical point in the joint density of states (that is, as a consequence of the highest valence and lowest conduction bands becoming parallel at a point along the $\Lambda$ symmetry axis). In pure

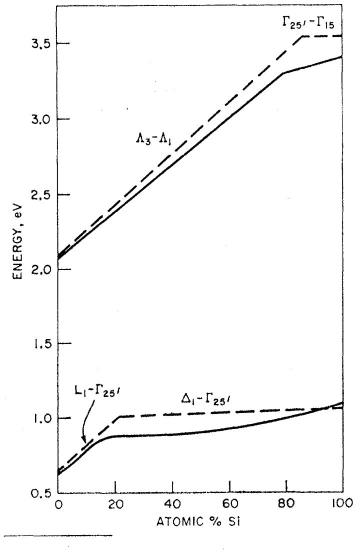

FIG. 5. Plots of energy gap and first reflectivity peak as a function of silicon concentration. The experimental results (Refs. 4 and 8) are indicated by solid lines and our theoretical results by broken lines.

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Si the equivalent peak arises from a $\Gamma_{25'}-\Gamma_{15}$ transition. As can be seen from Figs. 1 and 2 the $\Lambda_3-\Lambda_1$ is responsible for the peak provided $\Gamma_{2'}$ lies below $\Gamma_{15}$, but when the situation becomes reversed the $\Gamma_{25'}-\Gamma_{15}$ transition determines the peak. Hence, our interpretation of the discontinuity in slope is as follows: As Si is added to the alloy $\Gamma_{2'}$ moves up sharply and the $\Lambda_3 \rightarrow \Lambda_1$ critical point energy increases rapidly; however, at 79% Si, $\Gamma_{2'}$ must cross $\Gamma_{15}$ and the latter level which is less sensitive to further addition of Si produces the observed peak. Since the $\Gamma_{15}$ is an insensitive level, we would argue on the basis of this interpretation that the first reflectivity peak in Si should have a small pressure shift compared with that in Ge.

In Table I the experimental pressure coefficients for the band edges are given together with our computed values. There is a noticeable discrepancy between the experimental and computed coefficients; however, considering that the approximations made in deriving the pseudopotential parameters under pressure are only very crude and involve estimating a small difference between two large numbers we cannot expect more than a qualitative agreement. The sensitive levels move in the same direction under pressure, as the experiments indicate, and the insensitive levels have pressure coefficients much closer to 0. The minimum at $\Delta_1$ has a small positive pressure coefficient in our calculation while the high-pressure experiments of Slykhouse and Drickamer[18] give a small negative coefficient. To overcome this difficulty would probably require a more accurate estimate of the pseudopotential parameters than can be obtained with the analysis in this paper or a completely self-consistent OPW calculation.

As a conclusive remark we wish to point out that the conduction states $\Gamma_{2'}$ and $L_1$ are particularly sensitive to small changes of the pseudopotential parameters because of the form of their secular equations, which depend on the symmetry of these states. This is true in the pseudopotential approximation as in the full OPW method, and is discussed in detail in a previous paper.[19]

TABLE I. Theoretical and experimental pressure coefficients for some band edges in Ge in units of eV $10^{-6}$ $kg^{-1}$ $cm^2$ relative to $\Gamma_{25'}$. The experimental values have been taken from Ref. 6.

| | $\Gamma_{2'}$ | $L_1$ | $L_{3'}$ | $\Lambda_1$[a] | $\Delta_1$ | $X_1$ | $\Gamma_{15}$ |
|---|---|---|---|---|---|---|---|
| Calculated | 20 | 11 | 0 | ~12 | 3 | 2 | 3 |
| Experimental | 12 | 5 | — | — | −2 | — | — |

[a] The pressure coefficients of the first reflectivity peak attributed to $\Lambda_3 \rightarrow \Lambda_1$ is nearly the same as $\Lambda_1$, i.e., ~12 in the above units. The experimental value, which has been kindly communicated to the author by Dr. Paul is ~7.5 [R. Zallen, W. Paul, and J. Tauc, Bull. Am. Phys. Soc. **7**, 185 (1962)].

The strong dependence of the sensitive states on the space average of the potential and on the "core shifts" was first pointed out by Herman and Skillman[20] and discussed by Phillips.[9] The pressure effect should be obtained correctly in a full OPW calculation by taking into account the dependence on the lattice constant of all the orthogonalization constants and the Fourier coefficients of the potential. If the terms in the matrix elements originating from the core states are in general more affected by a change in the lattice parameter than the corresponding terms originating from the crystal potential, we expect that a full OPW calculation would give results for the pressure effect qualitatively similar to the ones obtained in the present work not only for Ge but for all group IV elements and probably for the III-V compounds as well. A possibility of this kind would be of great interest in connection with the experimental observation of Paul[6] that the energy levels seem to behave in the same way under pressure in all of the compounds which crystallize in the zincblende structure.

## ACKNOWLEDGMENTS

The authors are grateful to Dr W. Paul, Dr. J. C. Phillips, Dr. M. Cardona, and Dr. H. Ehrenreich for their interest and encouragement. They are also indebted to Dr. F. Herman for stimulating comments and to Professor F. G. Fumi for a critical reading of the manuscript.

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