

Valence Band Structure of Germanium-Silicon Alloys

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The valence band structure of Ge-Si alloys was determined by a study of free-hole absorption spectra. The spectra reveal a Ge-like valence band structure with a continuous variation of the hole effective masses and spin-orbit splittings with composition. The variation of the hole effective masses can be qualitatively accounted for by assuming that the optical matrix elements which couple various conduction and valence bands are independent of composition. The observed spin-orbit splittings are in agreement with a simple model which employs the free atom spin-orbit splittings of pure Ge and Si and which has been successfully employed in estimating the spin-orbit splittings of the III-V compounds.

INTRODUCTION

THE present work was directed towards a study of the valence band structure of Ge-Si alloys as revealed by the optical absorption due to free holes. The spectra enabled one to identify three valence bands and to determine the ratios of the hole effective masses and the spin-orbit splittings. Analysis of the spectra reveal a Ge-like valence band structure for the alloys with a continuous variation of the hole effective masses and spin-orbit splittings with composition. The variation of the hole effective masses with composition can be qualitatively accounted for by assuming that the optical matrix elements which couple various conduction and valence bands are independent of composition. The observed spin-orbit splittings of the alloys are in agreement with a simple model which employs the free atom spin-orbit splittings of pure Ge and Si and which has been successfully employed in estimating the spin-orbit splittings of the III-V compounds.¹

Earlier experimental work on the Ge-Si alloys employing optical absorption^{2,3} and transport⁴⁻⁶ measurements delineated the variation with composition of some of the major conduction and valence bands. These measurements have shown that the disordered alloys of Ge-Si have a distinct band structure with a continuous variation of energy gaps in going from pure Ge through the alloys to pure Si. There is no evidence of any tailing of the densities of states into the forbidden gap due to disorder.⁷ The present and past interest in this alloy system is that the main features of the band structure of Ge and Si are known from a wide variety of experimental measurements and theoretical considerations; consequently, it is possible to gain insight into the band structure of the disordered alloys by reference to the properties of the constituent elements.⁸

Several years ago, cyclotron resonance absorption experiments⁹ were reported on the Ge- and Si-rich ends of the alloy system; although resolved lines were observed, the resolution was rather poor due to scattering, and, consequently, it was not possible to determine if the curvatures of the energy bands varied with alloying. Recently our knowledge of the band structure of Ge, Si, and their alloys have been extended by a study of the fundamental reflecting spectra¹⁰ which have given information about the upper conduction bands.

EXPERIMENTAL TECHNIQUES

The samples used in these measurements were *p*-type samples of various compositions of Ge-Si alloy doped with shallow acceptor concentrations to yield free-hole concentrations of the order of $10^{17}/\text{cm}^3$. Samples in the range of composition from 0 to 20% Si were single crystals, and again single in the range from 70 to 100% Si. In the intermediate composition range, the samples were coarse polycrystalline. The method of preparation of the alloys depended upon the composition range.¹¹ Low and intermediate Si content samples were grown in a horizontal boat with suitable adjustment of the initial charge to yield the required composition; high Si content samples were grown by vertical pulling. The compositions were determined by x-ray techniques using the data of Johnson and Christian² and were determined to an accuracy of 1% of the amount present. The samples were selected for homogeneity of composition. In the range of composition where both single-crystal and polycrystalline samples were available, measurements of the absorption spectra on both types of samples yielded identical results, justifying the use of polycrystalline samples.

Hall measurements were made on samples selected from sections immediately adjacent to the samples used for the optical measurements to determine the hole concentrations. Table I gives the pertinent Hall and composition data for all the samples used in these

¹ R. Braunstein and E. O. Kane, *J. Phys. Chem. Solids* **23**, 1423 (1962).

² E. O. Johnson and S. M. Christian, *Phys. Rev.* **95**, 560 (1954).

³ R. Braunstein, A. R. Moore, and F. Herman, *Phys. Rev.* **109**, 695 (1957).

⁴ M. Glicksman, *Phys. Rev.* **100**, 1146 (1955); **102**, 1496 (1956).

⁵ M. Glicksman and S. M. Christian, *Phys. Rev.* **104**, 1278 (1956).

⁶ A. Levitas, *Phys. Rev.* **99**, 1810 (1955).

⁷ R. H. Parmenter, *Phys. Rev.* **97**, 587 (1955).

⁸ F. Herman, *Phys. Rev.* **95**, 847 (1954).

⁹ G. Dresselhaus, A. F. Kip, Han Ying Ku, G. Wagoner, and S. M. Christian, *Phys. Rev.* **100**, 1218 (1955).

¹⁰ J. Tauc and A. Abraham, *J. Phys. Chem. Solids* **20**, 190 (1961).

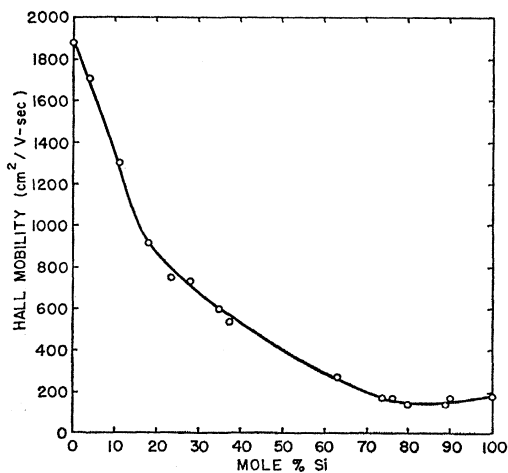
¹¹ S. M. Christian (private communication).

TABLE I. Hall data for *p*-type germanium-silicon alloy crystals at 295°K.

Crystal	Atomic percent silicon	$p = 10^{16}/\text{cm}^3$	$\frac{\mu_H}{\text{cm}^2/\text{V-sec}}$
Ge-1498P	0	5.0	1850
GS-3-10	4	2.1	1710
GS-3-22	11	1.6	1300
GS-5-10	18	3.0	916
GS-5-20	23	3.6	752
GS-5-27	28	3.1	728
GS-5-36	35	3.0	592
GS-5-49	37	3.0	537
D-186-1	63	4.0	275
SS-618-3	74	1.7	178
SS-618-2	76	17.0	172
SS-602-C	80	16.0	142
SS-602-B	89	16.0	139
SS-602-A	90	14.0	173
S-1076	100	50.0	180

measurements; the Hall mobilities are plotted in Fig. 1. It is seen that the Hall mobility is a monotonic function of composition and the mobility is determined by the composition and not by the differences in impurity concentration in each sample.

The absorption measurements were performed using a single-beam Perkin-Elmer monochromator with NaCl and CaF₂ optics for optimum resolution in appropriate spectral regions. The transmission was measured by the conventional sample-in-sample-out technique. In order to facilitate the reduction of the data to absorption coefficients as a function of wavelength, some automation of the data was employed. To obtain transmission as a function of wavelength for a sample using a single-beam monochromator, it is usually necessary to record the transmitted signal with the sample present in the beam (*I*), and then with the sample removed from the beam (*I*₀), and finally to compute the percent transmission *I*/*I*₀ point by point. This conversion was performed with the aid of a simple Ohm's law analog computer mounted directly on the recorder with $i = E/R$

FIG. 1. Hall mobility of *p*-type Ge-Si alloy.

$= I/I_0 =$ percent transmission, where *i*, *E*, and *R* are the current, voltage, and resistance of the network selected by appropriate values of *I* and *I*₀. First *I* vs wavelength was recorded and, then, the recorder chart rolled back to the starting point and *I*₀ vs wavelength recorded on the same chart. Wavelength marker pips were indicated at discrete intervals on both recordings. At the completion of the *I* and *I*₀ runs, the chart was again returned to the starting point. The output of the above Ohm's law network was then recorded with pointers manually selecting appropriate *I*~*E* and *I*₀~*R* values at discrete wavelength marker pips, yielding a histogram-like representation of *i*= percent transmission vs wavelength on the chart. The percent transmission was also fed to a digital printer which printed a numerical record of percent transmission corresponding to the graphic display of the recorder.

Analytical representations of the monochromator calibration curves were fitted using known absorption

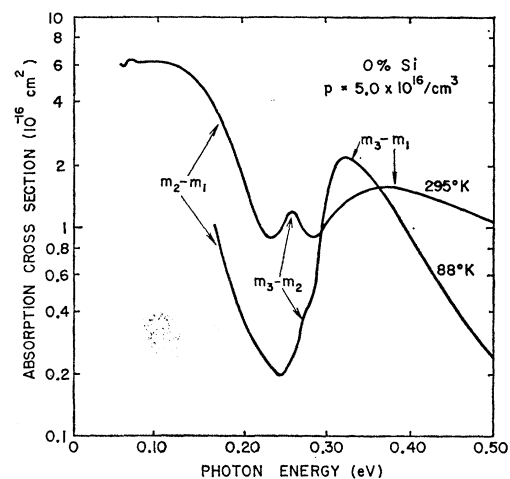


FIG. 2. Free-hole absorption spectra of pure Ge.

bands following the procedures given by McKinney and Friedel.¹² A program for the IBM-650 computer was prepared that contained the calibration curves and the analytical expressions for obtaining absorption coefficients from transmission data. The following input data for a given sample was supplied: % transmission as a function of marker pip, prism used, thickness of sample, and the reflectivity of the sample. The computer output yielded a typed record of absorption coefficient versus wavelength. The reflectivity coefficients were determined by measuring the transmission to the long-wavelength side of the absorption edge of intrinsic material for each composition and assuming that the transmission was limited by the reflectivity of the sample.

¹² D. S. McKinney and R. A. Friedel, J. Opt. Soc. Am. **38**, 222 (1948).

EXPERIMENTAL RESULTS

The free-hole absorption spectra for *p*-type Ge at 295 and 88°K are shown in Fig. 2. The spectra are similar to that previously reported for pure Ge,^{13,14} and interpreted by Kahn¹⁵ as due to hole transitions between three different valence bands. In Fig. 3 we have drawn schematically the valence band structure of Ge. One might expect to observe three absorption bands for *p*-type material due to transitions between these valence bands as seen for the following considerations. The electric dipole matrix element which vanishes for transitions between the bands at $\mathbf{k}=0$, where the bands have the same parity, is assumed to be proportional to \mathbf{k} , so that the transition probability as one moves off $\mathbf{k}=0$ increases proportionally to \mathbf{k}^2 . The absorption cross section, for each transition, increases rapidly at the absorption limit due to the \mathbf{k} dependence of the matrix element and then decreases at high values of \mathbf{k} due to the exponential decrease in the occupancy of states at high \mathbf{k} values.

In Fig. 3 the band labeled m_1 is the heavy-hole band, the band m_2 is a light-hole band, and m_3 is a band split off by spin-orbit splitting, which is the intermediate-hole band. Consequently, for the Ge spectra in Fig. 2, the band at 0.35 eV is considered to be due to transitions between band m_3 and band m_1 with a long-wavelength limit at 0.29 eV which corresponds to spin-orbit splitting at $\mathbf{k}=0$. The band at 0.24 eV is interpreted as due to transitions between m_3 and m_2 and has a short-wavelength limit also at 0.29 eV. The onset of the absorption band at 0.20 eV which increases as the photon energy decreases is considered to be due to transitions between the m_2 band and the m_1 band. As the temperature is decreased, the m_3 - m_1 band sharpens and is displaced toward lower energy while the intensity of

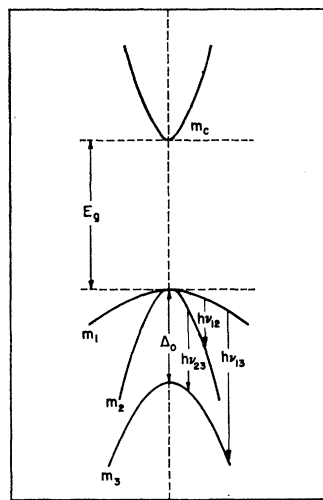


FIG. 3. Schematic diagram of the valence band structure of Ge at $\mathbf{k}=0$.

¹³ H. B. Briggs and R. C. Fletcher, Phys. Rev. **91**, 1342 (1953).

¹⁴ W. Kaiser, R. J. Collins, and H. Y. Fan, Phys. Rev. **91**, 1380 (1953).

¹⁵ A. H. Kahn, Phys. Rev. **97**, 1647 (1955).

the m_3 - m_2 band decreases markedly. The decrease in the m_3 - m_2 transition with temperature is due to the decreased hole population in the light-hole band, i.e., the light holes are coalescing into the heavy-hole bands.

Figures 4, 5, and 6 show the free-hole spectra of various compositions of the Ge-Si alloy system. Figure 7 shows the free-hole absorption spectra of a sample of pure Si. It should be noted that the general features of the spectra of pure Ge are retained in the alloy compositions up to 37% Si in Ge. In fact, the spectra of the Ge-rich alloys are very similar to that of pure Ge except for a general displacement of the spectra toward lower energies. In the above figures of the free-hole absorption spectra, we have plotted the absorption cross sections as ordinates, that is, the absorption coefficient divided by the free-hole concentration. It is seen, in general, that the absorption cross sections for the various bands are, to first order, independent of composition. In Figs. 8 and 9, we have plotted a superposition of the absorption

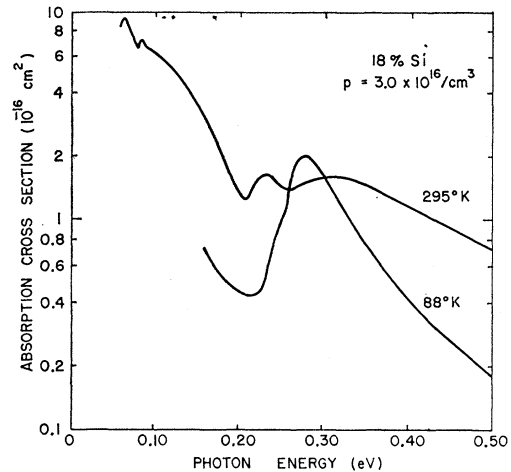


FIG. 4. Free-hole absorption spectra for a Ge-Si alloy with 18.0% Si.

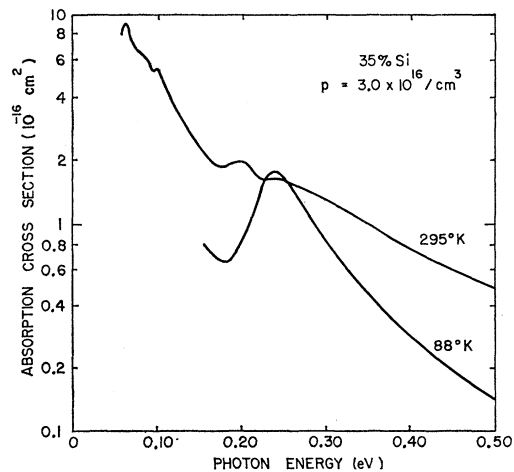


FIG. 5. Free-hole absorption spectra for a Ge-Si alloy with 35.0% Si.

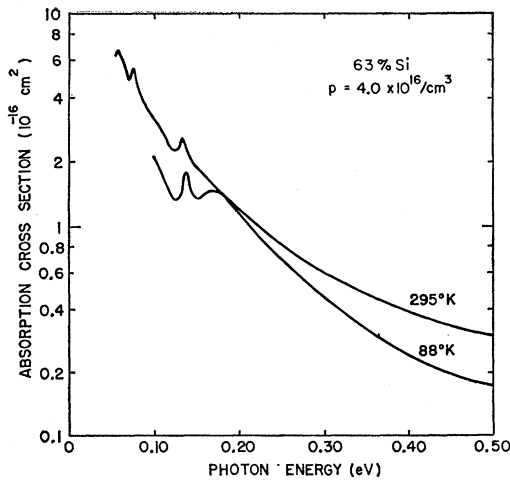


FIG. 6. Free-hole absorption spectra for a Ge-Si alloy with 63.0% Si.

bands obtained at room and nitrogen temperatures, respectively, for the complete alloy system. The absorption coefficients have been plotted on a logarithmic scale and with each spectra displaced relative to the others for the purposes of graphic representation. The absorption cross section = $2 \times 10^{-16} \text{ cm}^2$ is indicated by horizontal lines on the curves in Fig. 8, while the corresponding lines in Fig. 9 indicate cross sections = $1 \times 10^{-16} \text{ cm}^2$; consequently, if one wishes to compare the relative intensities, it is necessary to displace all the spectra to the same point using the indicated logarithmic scales.

From the above superposition, one can distinguish three distinct transitions up to the composition of 37% Si in Ge at room temperature. In the composition range from 63 to 100% Si, at room temperature, it is basically not possible to identify the free-hole absorption spectra characteristic of the inter-valence band transitions. The major shapes of the absorption bands at the Ge-rich end

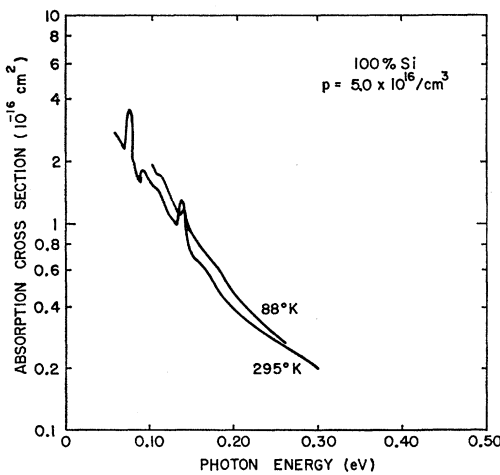


FIG. 7. Free-hole absorption spectra for pure Si.

of the system are similar to that of pure Ge, and, consequently, one may infer that the valence band structure of the alloys are similar to that of pure Ge. By referring to Figs. 2, 8, and 9 and the schematic diagram of the valence band structure in Fig. 3, we may designate the transitions in Ge and the alloys as follows: Starting at high photon energies, the first peak can be considered as due to transitions between the m_3 and m_1 band, the sec-

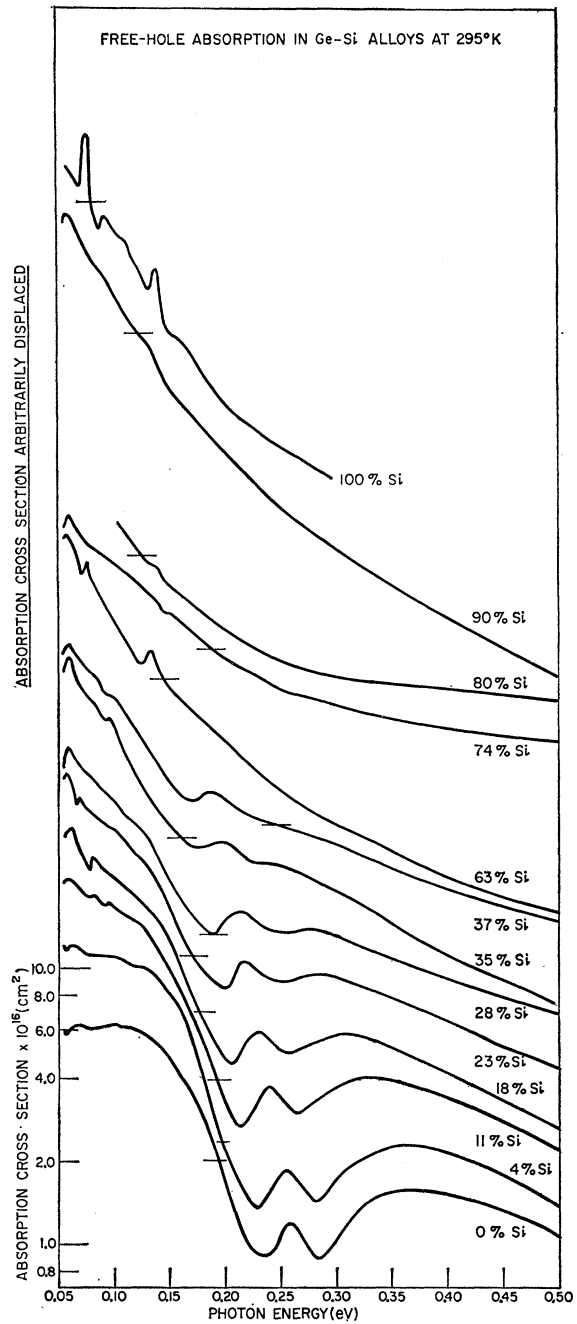


FIG. 8. Free-hole absorption spectra for Ge, Si, and Ge-Si alloys at 295°K.

ond peak as transitions between m_3 and m_2 , and finally the onset of the low photon energy absorption as due to transitions between m_2 and m_1 . There are changes in the ratios of the relative heights of the bands, in particular one sees that the m_3-m_2 transition increases in intensity relative to the m_3-m_1 transition as the Si content is increased. We shall show that the shifts of the spectra with composition and temperature can be accounted for by variations of the hole effective masses and the spin-orbit splittings from that of pure Ge.

For photon energies less than 0.15 eV, it is seen in Figs. 8 and 9 that there is fine structure superimposed upon the m_2-m_1 transitions which are seen much more distinctly in pure Si. This structure is also present in intrinsic material. This spectrum is due to intrinsic lattice vibrational absorption and the identification of these bands is given elsewhere.¹⁶ The band at 0.14 eV at the nitrogen temperature run for 63% Si is not associated with free-hole absorption but is due to the vibrational spectrum of an oxygen impurity.¹⁶ This band persists into the 100% Si composition, as one can see from Figs. 8 and 9.

INTERPRETATION OF THE SPECTRA

We have seen that through part of the composition range of the Ge-Si alloys, three absorption bands are observed in *p*-type material which have a characteristic shape and temperature dependence very similar to that of pure Ge. Consequently, one might infer that the alloys have a valence band structure very similar to that of pure Ge. It is possible to derive the valence band parameters such as the ratios of the hole effective masses and the spin-orbit splittings from the positions of the bands of the Ge-rich alloys.

Kahn¹⁵ has shown that the approximate shapes and positions of the free-hole absorption bands in Ge can be accounted for by fitting the effective hole masses and the spin-orbit splitting as parameters. However, this theory assumes spherical energy surfaces and, consequently, cannot account for the shape of the band to the high-energy side of the m_3-m_1 transition. The shape of the m_2-m_1 transition is also markedly determined by the shape of the bands away from $\mathbf{k}=0$ and cannot be accounted for by the simple theory. The exact shape of the bands reflects the nonparabolic nature of the energy surfaces. However, the average hole effective masses determined from cyclotron resonance measurements can reasonably account for the positions and temperature dependence of the free-hole absorption peaks in Ge since these are the masses that indicate the curvatures of the valence bands close to $\mathbf{k}=0$.

The position of the peak of the m_3-m_1 transition and the m_3-m_2 transition for Ge shown in Fig. 2, at a given temperature, are primarily determined by the effective hole mass ratios of these bands¹⁵ as well as by the spin-orbit splitting. Consequently, by measuring the tem-

¹⁶ R. Braunstein, following paper [Phys. Rev. **130**, 879 (1963)].

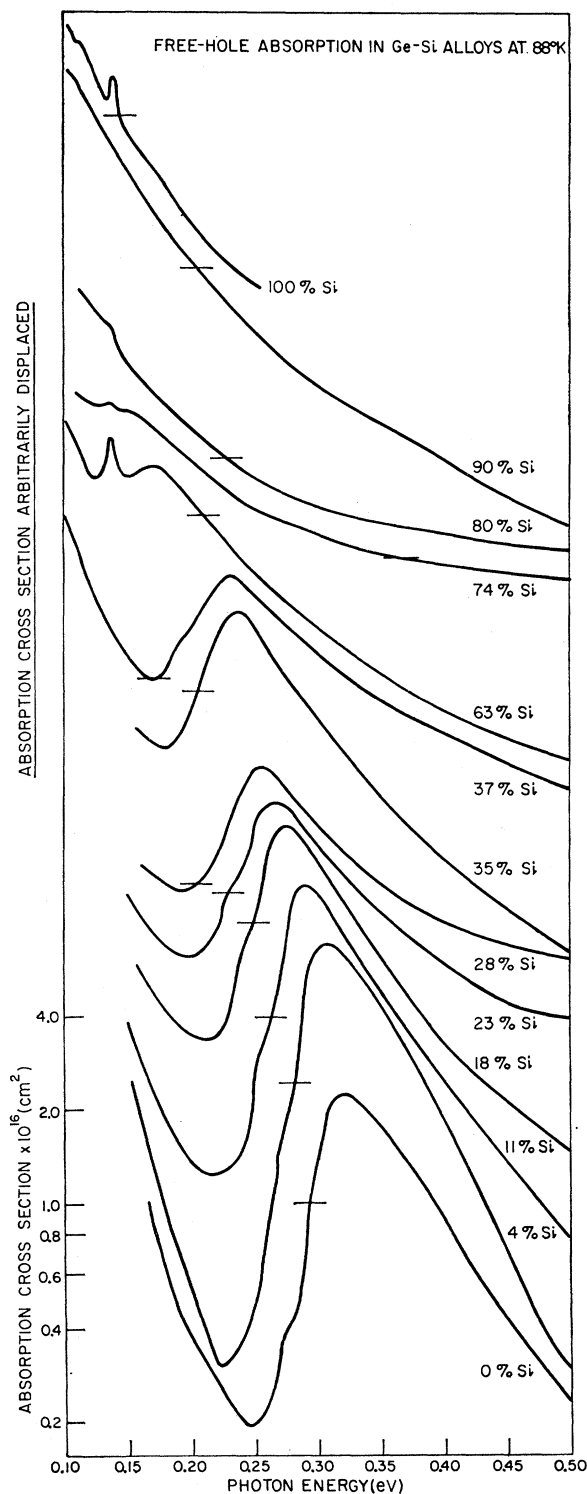


FIG. 9. Free-hole absorption spectra for Ge, Si, and Ge-Si alloys at 88°K.

perature dependence of the position of the m_3-m_1 transition, one can hope to calculate the effective mass ratio m_1/m_3 . If this is done for the Ge spectra, one ar-

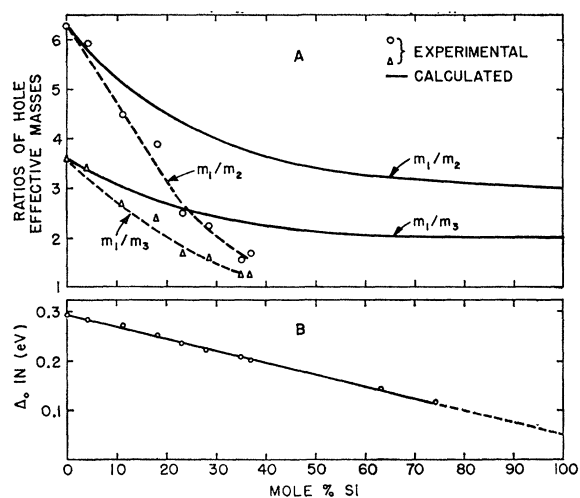


FIG. 10. The hole effective mass ratios in Ge-Si alloys are shown in curve A. The spin-orbit splittings are shown in curve B.

rives at an effective mass ratio $m_1/m_3 = 3.6$ which agrees extremely well with cyclotron resonance data.¹⁰ In a similar manner, by studying the temperature dependence of the m_3-m_2 transition one could obtain the ratio of m_2/m_3 . However, the m_3-m_2 transition is lost as one decreases the temperature and becomes less distinct as we increase the alloy composition as can be seen in Figs. 8 and 9. Since one may assume a mean value theorem for the holes, that is $1/m_3 = \frac{1}{2}[1/m_1 + 1/m_2]$, and since the spin-orbit splitting is less than the energy gap, it is possible to derive the ratio m_1/m_2 from a measurement of ratio m_1/m_3 . If this is done for Ge, we find $m_1/m_2 = 6.3$ which is again in good agreement with the cyclotron resonance value.⁹

Since it has been possible to derive the hole effective mass ratios of Ge from the absorption peaks which correlate with the cyclotron resonance data and since the shapes of the absorption spectra of the alloys are very similar to that of pure Ge, it seems justified to derive the m_1/m_3 ratios in the alloy system in the same manner as was done in pure Ge. The ratio m_1/m_2 can then be derived using the mean value theorem for the holes. The spin-orbit splitting can also be obtained as a parameter in fitting the observed spectra to the above spherical model.

Kane¹⁷ has calculated the shapes of the free-hole absorption spectra of Ge and has obtained a reasonable fit with experiments by including the nonparabolic nature of the valence bands. However, to perform the inverse operation in the alloys, that is to derive the nonparabolic nature of the bands from the shapes of the absorption spectra, does not seem to be a fruitful procedure.

The trough between m_3-m_1 and m_3-m_2 transitions is another measure of the spin-orbit splitting in Ge and the alloys. From Figs. 8 and 9, it is seen that as the Si end of the system is approached, the trough shifts

toward lower energies, reflecting the smaller spin-orbit splitting in Si as compared to Ge. However, this point becomes less distinct at higher compositions of Si. Since the shapes of the m_3-m_1 transitions are essentially maintained in the alloys and pure Ge, one may take the position of this peak as a measure of the spin-orbit splitting. In pure Ge the spin-orbit splitting is 0.29,¹⁷ and the peak of the m_3-m_1 transition occurs at 0.31 at liquid-nitrogen temperature. Consequently, the m_3-m_1 transition is removed from the spin-orbit splitting value by 0.02 eV. Assuming that this is also true in the alloys, we may obtain another determination of the spin-orbit splitting.

In Fig. 10 are plotted the ratios of m_1/m_3 obtained from the shift of the peak of the m_3-m_1 transition with temperature using the theory of Kahn¹⁵; the ratios m_1/m_2 derived from the mean value theorem are also shown in the figure. There is a continuous variation of these effective mass ratios with composition. It was only possible to obtain the mass ratios up to 37% Si, mainly because it was not possible to measure the temperature dependence of the position of the peak of the m_3-m_1 transition beyond this region. The experimental curves are indicated by dashed lines. The ratios m_1/m_2 and m_1/m_3 approach unity at 37% Si indicating that the curvatures of the light- and heavy-hole mass bands are approaching each other.

In Fig. 10 are shown the spin-orbit splittings as determined from the positions of the peaks of the m_3-m_1 transitions at liquid-nitrogen temperature. The spin-orbit splittings obtained as a parameter in determining m_1/m_3 agree within experimental errors with the above determinations. If one extrapolates the curve to pure Si, one obtains a value of 0.045 eV for this splitting.

THEORY AND DISCUSSION

In this section we shall attempt to account for the main band structure parameters of the alloys shown in Fig. 10 which were derived from the spectra. Namely, we shall account for the variation of the spin-orbit splitting in the alloy system and the ratios of the hole effective masses.

Spin-Orbit Splittings

The spin-orbit splitting of Ge and Si can be estimated with the help of the free-atoms splitting as obtained from atomic spectra, since the main effect of the solid is to alter the normalization of the wave function with higher order spherical harmonics. In Ge, the spin-orbit splitting in the solid is¹⁷ 0.29 eV as compared to 0.20 eV in the free atom, reflecting this change in normalization. In the solid, the Si spin-orbit splitting is 0.044 eV as determined by Zwerdling *et al.*¹⁸ from the observation of internal impurity levels in *p*-type Si. This is to be compared with the free-atom splitting of ~ 0.028 eV,¹

¹⁷ E. O. Kane, J. Phys. Chem. Solids 1, 83 (1956).

¹⁸ S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Letters 4, 173 (1960).

again reflecting the same enhancement of the spin-orbit splitting in the solid.

For the III-V compounds, it is possible to estimate the spin-orbit splitting at $\mathbf{k}=0$ by a relatively simple model, making use again of the free-atom splitting of the constituent elements. However, the partial ionic character of the bonding in the III-V compounds indicates that one may expect a valence electron at $\mathbf{k}=0$ to spend a different time around a cation and an anion state. If one assumes that a valence electron at $\mathbf{k}=0$ spends 35% of its time at a III atom site and 65% of its time at a V atom site, and one assumes the same normalization factor for Ge, namely 29/20, in going from the free atom to the solid, it has been possible to estimate the spin-orbit splittings of all the III-V compounds which are in good agreement with experiment.¹

In the case of the Ge-Si alloys, one would expect the spin-orbit splitting to be primarily determined by the time a hole spends at a Ge and Si site; since the bonding of Ge and Si are homopolar, one would expect that there is an equal probability for a hole to spend time at a Ge or Si site. If one assumes the same normalization factor for the alloys as for pure Ge and pure Si, the spin-orbit splitting of the alloy will be weighed proportional to the composition. This model predicts that the spin-orbit splitting in the alloys should be a linear function of composition.

Figure 10 shows the spin-orbit splitting as a function of composition in the Ge-Si alloy system from pure Ge to 74% Si. If we extrapolate the spin-orbit splittings of the alloy system to pure Si, we obtain 0.045 eV which is in good agreement with the value obtained by Zwerdling *et al.*¹⁸ The fact that there is a linear variation of the spin-orbit splitting in going from pure Ge to pure Si indicates that the normalization factor in the alloy system is similar to that of pure Ge and pure Si and that a hole has an equal probability of spending time at a Ge and Si site.

The reflectivity spectra of Ge-Si alloys exhibit a doublet structure⁹ in the first fundamental reflectivity peak in Ge and up to an alloy composition of 35% Si in Ge; this doublet structure has been interpreted as the splitting of the valence band near the edge of the zone at the point L_3 . The spin-orbit splitting near the Brillouin zone boundary is expected to be approximately $\frac{2}{3}$ of the splitting at the center of the zone.¹⁹ In the range of composition where the free-hole absorption data and the reflectivity data overlap, the spin-orbit splittings are in agreement within the experimental errors of the respective measurements.

The spin-orbit splitting in SiC has been determined to have an upper limit of ~ 0.008 eV and has been shown to be determined by the fractional time an electron spends in the Si and C sublattice.²⁰ The measured spin orbit¹⁸ in Si is 0.044 eV, while the diamond splitting can be estimated to be ~ 0.004 eV from atomic spectra.

Since the effective charge for SiC is ~ 0.94 with the excess electronic charge on the C atom,²¹ it is expected that the SiC spin-orbit splitting would be closer to the C rather than the Si value. Thus, although Si, Ge, and C are all column IV elements, the Ge-Si alloy splittings reflect the homopolar bonding while the SiC values reflect the ionic character of the bond.

Hole Effective Masses

Previous optical measurements^{2,3,9} on the alloys have shown that the conduction band structure of the alloys is similar to that of pure Ge and Si except for differences in the energy separations of the various bands. The free-hole absorption spectra observed in the present work have indicated that the valence structure of the Ge-Si alloys are also similar to that of pure Ge and Si. We shall now attempt to account for the variation of the hole effective masses with composition shown in Fig. 10. As we have seen, the hole effective-mass ratios for pure Ge, obtained from an analysis of the free-hole absorption spectra, are in good agreement with the values obtained by cyclotron resonance. The cyclotron resonance experiments on the Ge- and Si-rich sides of the alloys¹⁰ did not have sufficient resolution to indicate a variation of effective masses with composition. Consequently, it is not possible to directly correlate these results with the ratios of the effective masses as derived from the present work. We shall, however, attempt to calculate the effective mass ratios in the alloys by an interpolation procedure using the parameters of pure Ge and Si.

The valence band structure of Ge is shown schematically in Fig. 3, where we have drawn the three valence bands as parabolas. However, cyclotron resonance measurements have indicated that bands m_1 and m_2 are not spherical energy surfaces but have warping, i.e., they are re-entrant surfaces. The warping in the surface of the m_2 band is quite small in Ge and Si; however, the warping in the m_1 band is appreciable. Therefore, the constant energy surfaces are given by expressions that are generalized surfaces of rotation. The general expressions for the valence band were given by Dresselhaus *et al.*²² and Elliot.²³

In the interest of mathematical simplicity, the constant energy surfaces of the three valence bands can be represented as though they were spherical surfaces having an average curvature given by the following expressions²⁴:

$$E_{m_1, m_2}(k) \sim -(\hbar^2/2m)[A \pm (B^2 + C^2/6)^{1/2}]k^2, \quad (1)$$

$$E_{m_3}(k) = -\Delta_0 - (\hbar^2/2m)Ak^2. \quad (2)$$

The $+$ and $-$ signs refer to band m_2 and m_1 , respec-

²¹ W. G. Spitzer, D. Kleinman, and D. Walsh, Phys. Rev. **113**, 127 (1959).

²² G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).

²³ R. J. Elliot, Phys. Rev. **96**, 280 (1954).

²⁴ F. Herman, Proc. IRE **43**, 1703 (1955).

¹⁹ L. M. Roth and B. Lax, Phys. Rev. Letters **3**, 217 (1959).

²⁰ W. J. Choyke and L. Patrick, Phys. Rev. **127**, 1868 (1962).

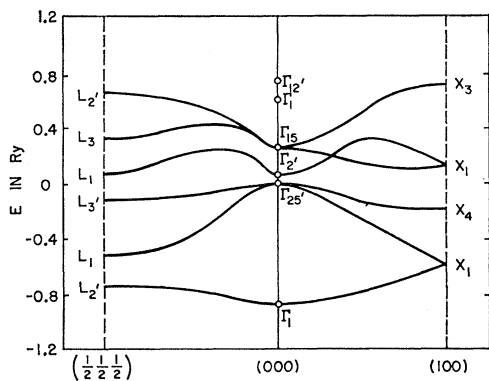


Fig. 11. The energy-band structure of Ge along principal direction according to Herman (reference 26).

tively. The use of the spherical approximation introduces negligible error in the case of the m_2 band, but has a significant error in the case of the m_1 band.

The constants A , B , and C are given by the following equations²⁵:

$$A = 1 + \frac{1}{3}(F + 2G + 2H_1), \quad (3)$$

$$3B = F + 2G - H_1, \quad (4)$$

$$3C^2 = N^2 - (3B^2), \quad (5)$$

$$N = F - G + H_1. \quad (6)$$

F , G , and H_1 can be expressed in terms of optical matrix elements between various bands at $\mathbf{k}=0$ and a series of energy denominators. F , G , and H_1 are given by the following equations:

$$F = \frac{\hbar^2}{2m} \frac{|\langle \Gamma_{2'} | \hat{p} | \Gamma_{25'} \rangle|^2}{E_0 - E_1}, \quad (7)$$

$$G = \frac{\hbar^2}{2m} \frac{|\langle \Gamma_{12'} | \hat{p} | \Gamma_{25'} \rangle|^2}{E_0 - E_2}, \quad (8)$$

$$H_1 = \frac{\hbar^2}{2m} \frac{|\langle \Gamma_{15} | \hat{p} | \Gamma_{25'} \rangle|^2}{E_0 - E_3}, \quad (9)$$

where E_0 , E_1 , E_2 , and E_3 refer to the energies of the $\Gamma_{25'}$, $\Gamma_{2'}$, $\Gamma_{12'}$, and Γ_{15} energy bands, respectively. These expressions are given by Phillips²⁵ and neglect the small contributions of higher bands of the same symmetry and also higher Γ_{25} bands.

Figure 11 shows the current energy band contours of pure Ge as have been calculated by Herman²⁶; Figure 12 shows the band structure of pure Si calculated by Kleinman and Phillips.²⁷ The band structures of Ge-Si alloys will be somewhere between that of pure Ge and Si and will be composition dependent. In order

²⁵ J. C. Phillips, Phys. Rev. **125**, 1931 (1962).

²⁶ F. Herman and S. Skillman, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961).

²⁷ L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960).

to calculate A , B , and C , and hence the effective masses for the three valence bands, it is necessary to know the value of the optical matrix elements and the energy differences between the various bands at $\mathbf{k}=0$ in Eqs. (7), (8), and (9). In view of the fact that the energy denominators and matrix elements are not known with sufficient accuracy, it is not possible to calculate F , G , and H_1 from these expressions. However, it appears that these optical matrix elements which are required to calculate the effective masses are effectively constant through the tetrahedrally valence types of crystals.²⁸ Measurements of direct interband transitions in groups IV, III-V, and II-VI semiconductors²⁹ further indicate the constancy of the optical matrix elements. Phillips²⁵ has shown that if the energy bands shift by only a few eV from one semiconductor to another, the approximate constancy of matrix elements can be used to estimate energy differences from effective mass data.

We shall now attempt to estimate the effective masses of the holes in the alloys by estimating the variation of the cyclotron resonance constants A , B , and C with composition from the experimental values of pure Ge and Si. An estimate of these constants in the alloys can be made by assuming that each of the optical matrix elements in Eqs. (7), (8), and (9) are constant throughout the Ge-Si alloys. The major variation in the constants in F , G , and H_1 , and hence, the effective hole masses are then primarily determined by the variations of the energy separation of various bands. Figure 13 shows some of the major energy gaps in Ge, Si, and Ge-Si alloys determined optically^{2,3,10,25,29}; the present determination of the split-off valence bands are included in the figure. Ehrenreich, Philipp, and Phillips²⁹ have delineated many other energy gaps in Ge and Si which have not been included in this figure. These measurements indicate that bands move linearly with composition. Consequently we may attempt to calculate the hole effective masses in the alloys by assuming a linear variation of $1/F$, $1/G$, $1/H_1$ with composition.

The experimental values of the band structure parameters A , B , and C in units of $\hbar^2/2m$ as derived from

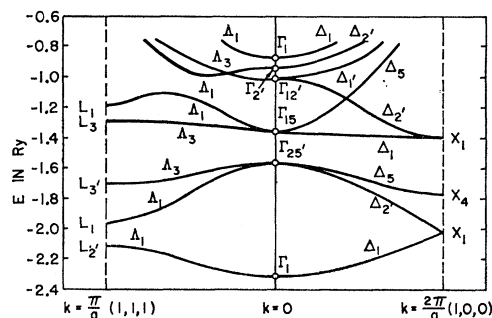


Fig. 12. The energy-band structure of Si along principal directions, as calculated by Kleinman and Phillips (reference 27).

²⁸ H. Ehrenreich, Suppl. J. Appl. Phys. **32**, 2155 (1961).

²⁹ H. Ehrenreich, H. R. Philipp, and J. C. Phillips, Phys. Rev. Letters **8**, 59 (1962).

cyclotron resonance absorption measurements and summarized by Herman²⁴ are as follows: For Si: $A=4.1$, $B=1.4$, and $C=3.7$; for Ge: $A=13.0$, $B=8.7$, and $C=11.4$. The Ge and Si cyclotron resonance constants were used to derive the ratios of m_1/m_2 and m_1/m_3 throughout the alloy system. One can actually derive the effective masses m_1 , m_2 , and m_3 as absolute quantities. However, since in the present experiments, it was only possible to obtain the ratios of the effective masses, we have plotted only the calculated ratios in Fig. 10. These curves are indicated by the solid lines and are to be compared with the dashed curves which are the experimentally derived ratios. The calculated variation of the hole mass ratios with composition is a monotonically decreasing function as we proceed from Ge to Si. The experimentally derived ratios are only in rough qualitative agreement with the calculated mass ratios. These quantitative differences may be due to deficiencies in the theory. The optical matrix elements may vary slightly in going through the alloy system. There may, in turn, be systematic errors introduced in the determination of the experimental mass ratios. The most that one can say is that a variation in effective masses of the hole bands as we move through the alloy system is indicated by the above simple model. These results are to be contrasted with the observations of cyclotron resonance⁹ where there was no evidence for the variation of effective masses with alloying, probably due primarily to the limitations in resolution of the experiments.

The experimental ratios of the hole effective masses shown in Fig. 10 are seen to approach unity at approximately 37% Si. This would indicate that the light-hole mass curvature and the heavy-hole mass curvature are approaching each other. Other optical measurements have yielded information that have a bearing on this observation. The first fundamental reflection peak of Ge and Ge-Si up to approximately 35% exhibited a doublet

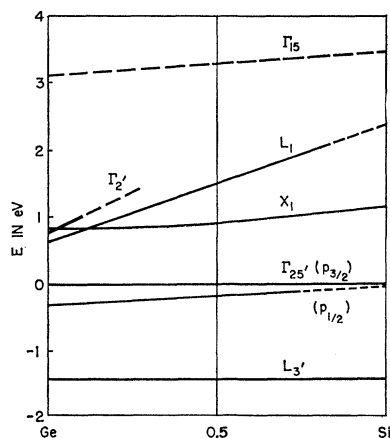


FIG. 13. The variation of important valence and conduction bands in Ge-Si including present measurements and the summary given by Phillips (reference 25) of previously experimentally determined optical absorption edges (references 2, 3, 10, and 29). The observed absorption edges are indicated by solid lines, while the extrapolations are shown by dashed lines.

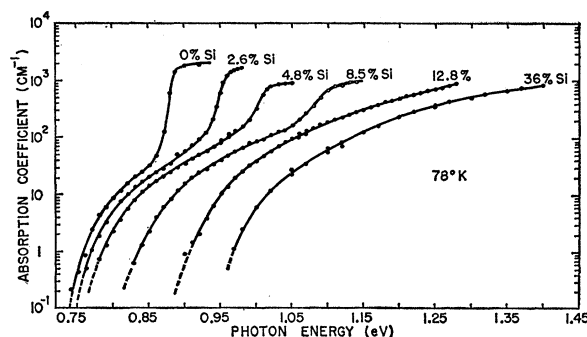


FIG. 14. Intrinsic absorption spectra in a series of Ge-rich Ge-Si alloys at 78°K as determined by Braunstein, Moore, and Herman (reference 3). In the samples up to 8.5% Si, the first rise in the absorption coefficient is due to indirect electronic transitions, while the second is due to direct electronic transitions. At larger Si composition there is no distinct separation of these transitions.

structure¹⁰ which was indicative of the spin-orbit splitting at the L_3 point of the heavy-hole band at the edge of the reduced zone. For greater Si content, the doublet structure could not be seen due perhaps to the decrease in the spin-orbit splitting. It is suggestive that if the heavy-hole mass band and the light-hole mass band curvatures were approaching each other throughout the Brillouin zone at 37% Si, as seems indicated by the present work, one would have expected the doublet due to the L_3-L_1 transition in reflectivity to disappear at this composition.

The work of Tauc and Abraham¹⁰ on the fundamental reflectivity has also shown that the first peak in the reflectivity spectra of Si corresponds to a different transition than that of Ge. Experimentally there is an abrupt break in the composition dependency of the shift of the first reflectivity peak beyond 77% Si. The theoretical evidence for this is that Phillips²⁵ has shown that the L_3 conduction band has a lower energy than the L_1 band in Si as compared to Ge. As we have previously noted in following the evolution of the valence band structure in Ge-Si alloys, it is not possible to distinguish any structure due to intervalence band transitions beyond 74% Si as can be seen from Figs. 8 and 9. The free-hole absorption spectra is very similar to that of pure Si. It is also of interest to note that at this point the temperature dependence of the absorption coefficient also reverses from that of Ge; on the Si end of the system, the absorption increases with decreasing temperature. It is suggestive that there may be a relationship between these changes and the changes in the valence band structure observed from the reflection measurements.

Electron Effective Masses at $k=0$

The fact that the optical matrix elements coupling the p -like valence and the s -like conduction bands are approximately constant in the III-V compounds can be used to calculate the electron effective masses for the conduction bands at $k=0$ which are in good agreement with the experimentally determined values.²⁸ In an

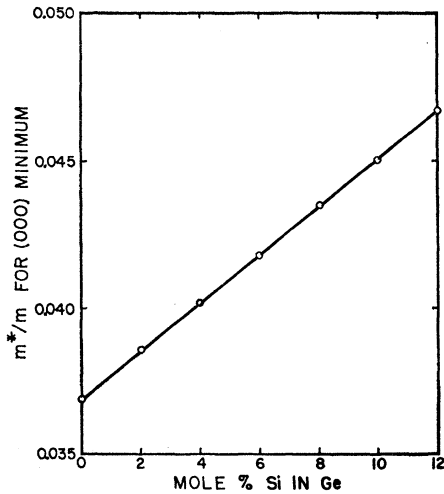


FIG. 15. The calculated electron effective masses for the $\mathbf{k}=0$ minima in Ge-Si alloys.

analogous fashion, we can derive the electron effective masses at $\mathbf{k}=0$ in the Ge-Si alloys. The electron effective masses, m_e , for Ge are given by the following expression³⁰:

$$\frac{1}{2m_e} = \frac{1}{2m} + \frac{1}{m^2} \frac{3E_G + 2\Delta_0}{3E_G(E_G + \Delta_0)} |p|^2, \quad (10)$$

where $|p|^2$ is the optical matrix element squared, E_G is the band gap at $\mathbf{k}=0$, and Δ_0 is the spin-orbit splitting. If we use $E_G=0.90$ eV and $m_e=0.03m$ as determined by Roth *et al.*,³⁰ we can calculate $|p|^2$; assuming that $|p|^2$ is constant in the alloys, we can calculate m_e using Δ_0 determined from the present work, and E_G determined from previous³ work. Figure 14 shows the intrinsic absorption edges of the alloys.³ The calculated electron effective masses at $\mathbf{k}=0$ versus composition are shown in Fig. 15 up to 12% Si. It was not possible to measure the conduction band separation at $\mathbf{k}=0$ beyond 12% Si in the intrinsic optical absorption experiments since it is no longer possible to distinguish between direct and indirect transitions. In fact the intrinsic absorption edge for composition greater than 12% assume a Si-like character.

It is not clear why it is no longer possible to distinguish between direct and indirect transitions in the intrinsic absorption edges beyond 12% Si in Ge. Figure 11 shows the Ge band structure as calculated by Herman,²⁶ where it is seen that the $\Gamma_{2'}$ minimum is the lowest minimum at $\mathbf{k}=0$. Kleinman and Phillips²⁷ have indicated that the Γ_{15} minimum is probably lowest in Si; their Si band structure is shown in Fig. 12. Consequently, in moving from pure Ge to pure Si there is a point where the $\Gamma_{2'}$ and Γ_{15} bands cross. However, the crossing of these bands probably takes place at ~ 3 eV in the alloys which would occur at the Si-rich end of the

system as can be seen from Fig. 13 using the data of Ehrenreich *et al.*²⁹ This point might be clarified when the absorption due to vertical transitions is decomposed into a purely electronic component (direct vertical transitions) and an optical phonon-assisted component (indirect vertical transitions).³¹

CONCLUSIONS AND SUMMARY

The free-hole absorption spectra of the Ge-Si alloys have revealed that the valence band structure of the alloys is similar to that of pure Ge and Si. There was no evidence of tailing of the densities of states into the forbidden gap due to disorder as indicated by the similarity of the shapes of the absorption bands in the alloys with those of pure Ge. Analysis of the spectra indicates a continuous variation of the hole effective masses and spin-orbit splittings with composition.

The fact that spin-orbit splitting is a linear function of composition in going from pure Ge to pure Si is consistent with the model that one may estimate the spin-orbit splitting from the atomic spectra values. The enhancement of the splitting in going from the free-atom case to the solid is the same throughout the Ge-Si alloy system and there is an equal probability of a hole to occupy a Ge and Si site. This picture is similar to the treatment given for the III-V compounds¹ where a hole has a different probability of spending time on a column III or V site because of the partial ionic character of the bond. The fact that the normalization factor in the III-V compounds is the same as that of pure Ge, Si, and Ge-Si alloys indicates, to the experimental accuracy of this type of measurement, that it is the same in a large class of semiconducting compounds. The enhancement of the spin-orbit splitting of valence states in the crystal over the corresponding atomic value for Ge and Si have been estimated from theory.³²

It was possible to qualitatively understand the composition dependency of the effective hole masses in the alloys by using a simple spherical model for the valence bands and assuming that the optical matrix elements which couple various p - and s -like states are independent of composition. The major changes in the hole effective masses are then determined by the linear variation with composition of the various band separations. However, the experimental evidence that the light- and heavy-mass band curvatures are approaching each other at $\sim 37\%$ Si in Ge is not shown by this model. Magnetoresistance measurements on the holes could further clarify this point by indicating whether the two-carrier model necessary to account for the transport properties of p -type Ge is replaced by a one-carrier model at this composition.

The band structure of Ge-Si alloys have now been delineated by a wide variety of experiments. The measurements of intrinsic absorption edges,³ reflectivity in the fundamental region,¹⁰ and magnetoresistance meas-

³⁰ L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. **114**, 90 (1958).

³¹ W. P. Dumke, Phys. Rev. **108**, 1419 (1958).

³² L. Liu, Phys. Rev. **126**, 1317 (1962).

measurements⁴ have given information about the positions of the various conduction bands. The present work has delineated some of the valence band structure parameters. The phonon energies at the edge of the Brillouin zone have also been measured by observing multiple phonon absorptions in the lattice vibrational spectra.¹⁶ The availability of the above information makes the Ge-Si system a desirable one upon which to test various theoretical models of the band structure of disordered alloys.

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Lattice Vibration Spectra of Germanium-Silicon Alloys*

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The infrared lattice absorption spectra of germanium-silicon alloys were determined in the wavelength region from 8–48 μ and have been analyzed to obtain information on the lattice vibrational spectra of the disordered crystals. The evolution of the spectra was followed from pure germanium through the alloys to pure silicon and the major two-phonon combination bands were identified. The optical and acoustical frequencies near the edge of the reduced zone were determined throughout the alloy system by identifying equivalent bands in the alloys with those of pure germanium and silicon which were assigned by using neutron scattering data. The gross features of the spectra revealed a continuous variation of the positions, shapes, and the intensities of the absorption bands as a function of composition; however, the strongest germanium-like summation band ($TA+TO$) approaches but does not merge with the equivalent silicon-like band. It is possible to observe both of these bands simultaneously on samples near the central range of composition. The appearance of new bands, not present in either pure germanium or pure silicon, due to the addition of small amounts of silicon to germanium or vice versa, were identified as vibrational impurity bands. The relative insensitivity of the phonon energies with composition are in agreement with a previous determination of equivalent phonons involved in the indirect transitions of the intrinsic absorption edge. The results of the analyses of the lattice absorption spectra of germanium-silicon alloys are compared with various theoretical models that have been proposed for the vibrational spectra of disordered crystals.

IN this work, the infrared lattice absorption spectra of the germanium-silicon alloys were observed in the spectra region from 8 to 48 μ and were analyzed to obtain information on the lattice vibrational spectra of the disordered crystals. Although considerable experimental information has been accumulated in recent years regarding the vibrational spectra of regular crystals, correspondingly little experimental information is available concerning the vibrational spectra of disordered crystals. The theoretical understanding of the lattice vibrational spectra of regular crystals is sufficiently advanced in the case of germanium and silicon to enable one to calculate the lattice vibration dispersion curves^{1,2} which are in agreement with those experimentally determined by neutron scattering.^{3–6} The

theoretical methods that are employed for regular crystals depend intimately upon the periodicity of the regular lattice and cannot be directly applied to cases where small impurity concentrations are added to the solid or to the case of mixed crystals. It was the intent in undertaking this study of an infrared absorption spectra of a Ge-Si alloys to obtain some information on the vibrational spectra of disordered lattices that may serve as a spur to the theoretical studies of the problem and to serve as a check on future theoretical developments.

The Ge-Si alloy system was selected for study since the infrared lattice absorption spectra of germanium and silicon^{7–9} are known in considerable detail and, consequently, one can attempt to understand the spectra of the disordered lattice by reference to the spectra of the pure constituents of the alloys. This alloy system is also well suited for study since its electronic band structure is fairly well delineated both experimen-

* A preliminary report on this work was presented at a meeting of the American Physical Society, 1960 [Bull. Am. Phys. Soc. 5, 198 (1960)].

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³ B. N. Brockhouse and P. K. Iyengar, Phys. Rev. 111, 747 (1958).

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