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OPTICAL PROPERTIES OF SEMICONDUCTORS UNDER HYDROSTATIC PRESSURE—III

GERMANIUM-SILICON ALLOYS*

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Abstract—The optical absorption edge of a number of germanium–silicon alloys has been measured at room temperature as a function of hydrostatic pressure from 1 to 7000 kg/cm^2. The pressure variation of the energy corresponding to the edge $(dE/dP)_T$ varies continuously with composition from pure germanium to pure silicon. A break in this curve is found between 10 and 20 per cent silicon, consistent with an interpretation in which the (100) conduction-band minimum becomes lower than the (111) minimum as silicon content is increased.

1. INTRODUCTION

IN two previous papers,(1) data have been presented on the shift with pressure of the optical absorption edges in silicon and germanium. In this paper corresponding data for a number of alloys of the two elements will be discussed.

The band structure of germanium is shown in Fig. 1, and that of silicon in Fig. 2. The lowest conduction-band minimum in each of these materials does not lie at the center of the Brillouin zone, whereas, in each case, the valence-band maximum does. The onset of the optical absorption edge in both of these materials is therefore thought to be due to an indirect transition from the valence-band maximum to the conduction-band minimum, with a conduction-band minimum at (000) in both cases as a possible virtual state.

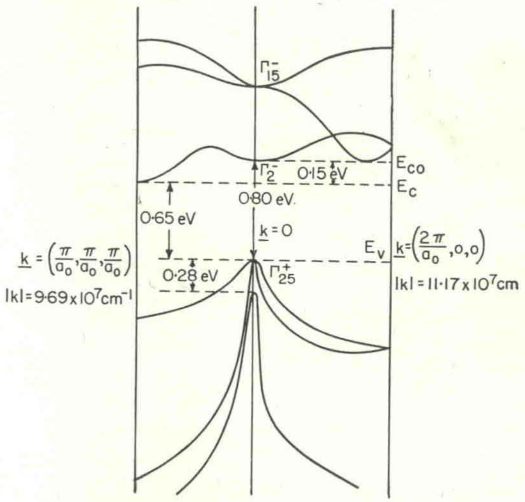

FIG. 1. Band structure of germanium.

PAUL and BROOKS(2) interpreted their measurements of the resistivity of germanium as a function of pressure in terms of an increase of the forbidden-gap width due to movement of the (111) conduction-band minimum upward§ with increasing pressure. Similar measurements on silicon(3) indicated a decrease in energy gap with increasing pressure, presumably because of the downward motion of the (100) minimum. This decrease

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§ "Upward" and "downward" in this paper will always mean relative to the valence-band maximum.

occurs at a much slower rate than that of the increase in germanium. On the basis of these measurements, the optical-pressure experiments already reported on germanium and silicon were undertaken. These measurements of the pressure change of the energy gap are consistent with the interpretation just given.

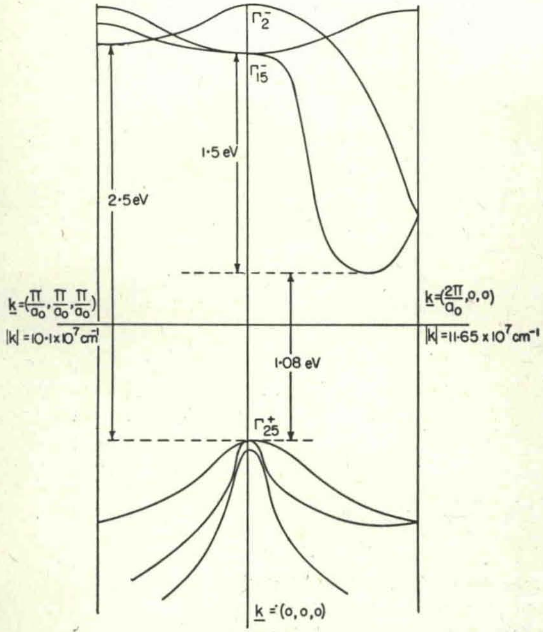

FIG. 2. Band structure of silicon. Adapted from an article by HARVEY BROOKS in *Advances in Electronics and Electron Physics*, Vol. 7. Academic Press, New York (1955).

JOHNSON and CHRISTIAN,⁽⁴⁾ and independently LEVITAS *et al.*,⁽⁵⁾ measured the energy gap of germanium–silicon alloys as a function of composition. The latter workers determined the forbidden gap from measurement of intrinsic resistivity versus temperature, while the former used an optical method. The two results differ considerably, but there is reason to believe that the optical determination is the more reliable.

JOHNSON and CHRISTIAN's curve of the energy-gap variation with concentration rises sharply with increasing silicon content to about 15 per cent, at which point a straight line of much smaller slope takes over. This measurement can be interpreted as a rapid upward motion of the (111) minimum as silicon is added to germanium. At about 15 per cent silicon both (111) and (100) minima occur at the same energy, while at higher concentrations the (100) minimum is lower and moves more slowly away from the valence band. The arguments for this view were summarized by HERMAN.⁽⁶⁾

More recent experiments on the optical gap width as a function of alloying indicate that neither region of the energy gap is linear⁽⁷,⁸⁾ with respect to composition. This conclusion is derived from a fit of a one-phonon model to the alloy absorption-edge data, in the manner of MACFARLANE and ROBERTS.⁽⁹⁾ The break occurs at roughly the same concentration as in the graph of JOHNSON and CHRISTIAN, but both regions are roughly parabolic in shape. The average phonon energy obtained on this basis, however, shows a rapid change only in the region of approximately equal concentration.

As will be seen, some conclusions can be drawn from measurements of the transmission as a function of pressure, using only the band model derived to date. Reasons will be given for our avoidance of using some particular theoretical model for the optical transitions.

2. METHOD

The samples used in these experiments were supplied through the generosity of RCA and Sylvania Products, Inc. No alloy above 18 per cent silicon was measured, with the exception of the pure silicon previously reported. The composition of the RCA alloy samples was deduced from spectrographic measurements* on nearby portions of the same alloy ingot.⁽¹⁰⁾ This composition can be checked by determining the half transmission wavelength, using a curve of the sort first found by JOHNSON and CHRISTIAN. We verified the composition of the RCA samples, and determined that of the Sylvania samples in this fashion.

The samples supplied by RCA had been selected on the basis of high long-wavelength transmission, whereas none of the material supplied by Sylvania exhibited a transmission higher than a few per cent. The magnitude of the transmission was taken as a criterion of the degree of perfection of the alloy crystals. On this basis, most of the Sylvania alloys, which were among the first to be produced, were

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* We are grateful to the RCA Laboratories for making this determination.

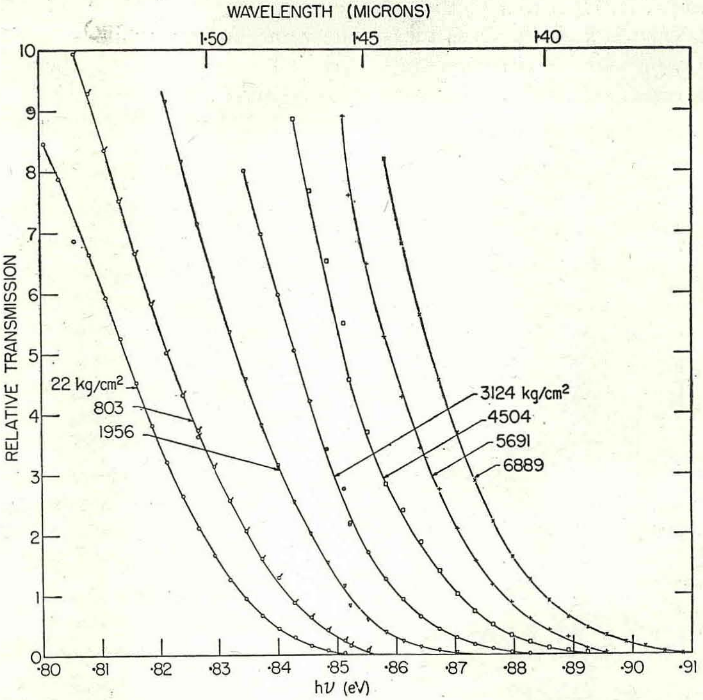


Fig. 3. Relative transmission of 3 per cent silicon in germanium alloy versus photon energy, at several pressures. Adapted from an article by Harvey Brooks in *Advances in Electronics and Electron Physics*, Vol. 7. Academic Press, New York (1955).

not used. One of the Sylvania samples which was used, also of low transmission, showed anomalous results, as will be discussed later.

The question of transmission also affected the decision regarding the method of measurement to be used. In the work previously reported on germanium,(1) the absorption constant of the material was obtained as a function of wavelength at each pressure. The absorption constants so derived were necessary for a discussion of the validity of theories pertaining to the shape of the absorption edge.

In the paper on silicon,(1) the discussion was based on the transmissivity of the samples, rather than the absorption constant, on the basis that none of the pertinent theories was well-enough established to recommend its application, and because no change of shape of the edge was observable.

Similar considerations pertain to the alloys. Furthermore, as mentioned earlier, the transmissivity of alloy samples can vary widely, for reasons which have not as yet been established. Selection of suitable samples depends on the assumption that the higher the transmission for a given composition, the better the samples. Thus, the samples examined should have a transmission approaching, but not necessarily equal to, the theoretical maximum.

Summarizing these arguments, we think there is sufficient doubt about the details of the alloy band structure, about the model to be used for the optical transitions, and about the quantitative significance of the absorption coefficients, so that all of the useful information about the pressure changes can be obtained from an examination of the results for the transmission.

The relative transmission of each sample was measured as a function of pressure at room temperature, in a manner similar to that used in the silicon experiments. A Perkin–Elmer spectrometer with a 300-line/mm grating was used for most of the experiments. A cooled lead sulfide cell served as

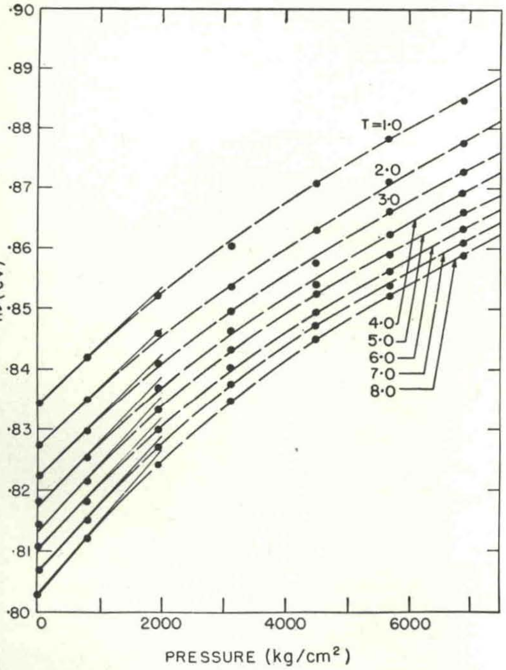


FIG. 4. Isotransmission plot of 3 per cent silicon in germanium alloy. Average initial slope = $1{\cdot}09\times 10^{-11}$ eV/dyne−cm^{-2}. Average final slope = $5{\cdot}71\times 10^{-12}$ eV/dyne−cm^{-2}.

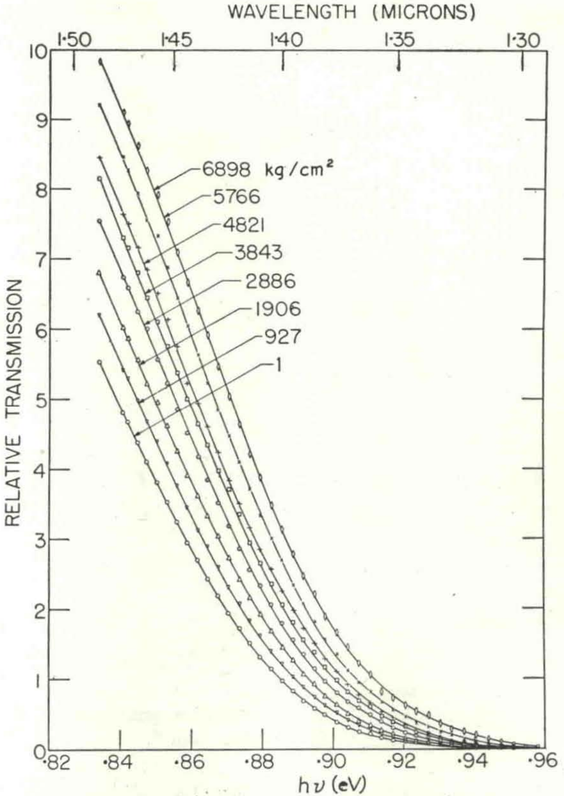


FIG. 5. Relative transmission of 9 per cent silicon in germanium alloy (RCA D106R) versus photon energy, at several pressures.

detector. Sample transmission was measured at hydrostatic pressures up to 7000 kg/cm^2.

3. RESULTS

The transmissions were normalized to an arbitrary value and plotted as a function of photon energy. From these graphs, isotransmission values of photon energy were determined as a function of pressure. Data for the various samples are shown in Figs. 3–15. Corresponding curves for germanium and silicon are presented for comparison in Figs. 16 and 17. The slope of the isotransmission plots is shown as a function of composition in Fig. 18. It is to be noted that, with the exception of the sample of 3 per cent silicon in germanium, all of the samples below about 18 per cent silicon in germanium exhibit a germanium-like slope, whereas at 18 per cent silicon no measurable slope was observed. At the silicon end, a negative slope is found.

4. DISCUSSION

As mentioned in the silicon paper,(1) the slope of the isotransmission curves can be interpreted in terms of the change of forbidden-gap width with pressure, particularly if no indication of change of shape of the absorption edge exists.

Thus, the graph of Fig. 18 indicates an increase of the forbidden gap with pressure up to a concentration somewhere around 18 per cent silicon. Beyond this percentage the gap appears to decrease with pressure.

This change-over is consistent with the absorption measurements of JOHNSON and CHRISTIAN(4) and BRAUNSTEIN.(7,8) We interpret the application of pressure and the addition of silicon as causing an upward movement of the (111) minimum. On the other hand, above the 18 per cent range, addition of silicon apparently causes a slower upward movement of the (100) band, while pressure causes the band to move at a slow rate

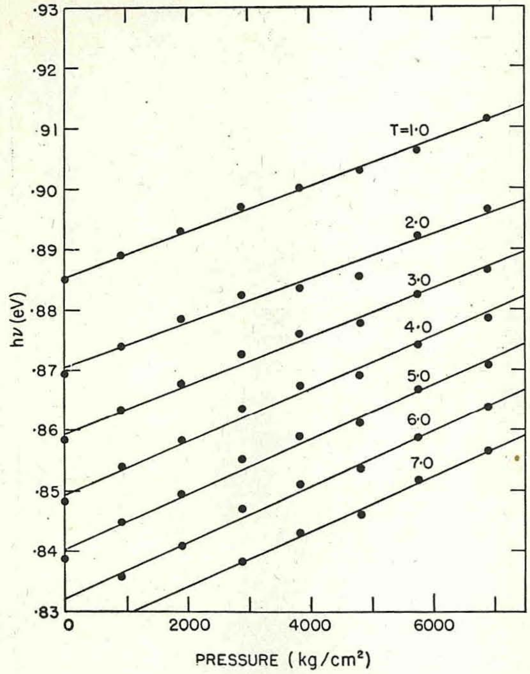


FIG. 6. Isotransmission plot of 9 per cent silicon in germanium alloy (RCA D106R). Average slope = $4 \cdot 31 \times 10^{-12}$ eV/dyne$-$cm^{-2}.

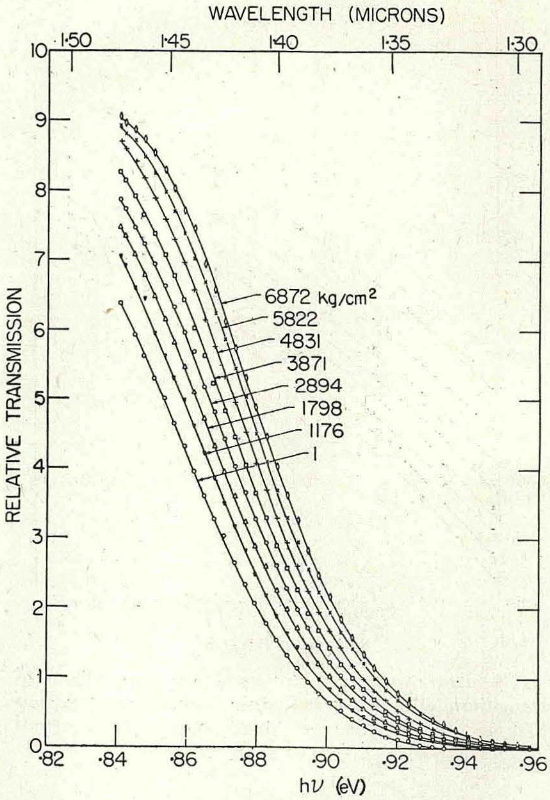


FIG. 7. Relative transmission of 11 per cent silicon in germanium alloy (RCA D106T) versus photon energy, at several pressures.

toward decreasing gap width. The difference between the gap change caused by decreasing the interatomic spacing through pressure and that caused by decreasing it through alloying stems from the change in potential caused by the substitution of silicon atoms for germanium ones.

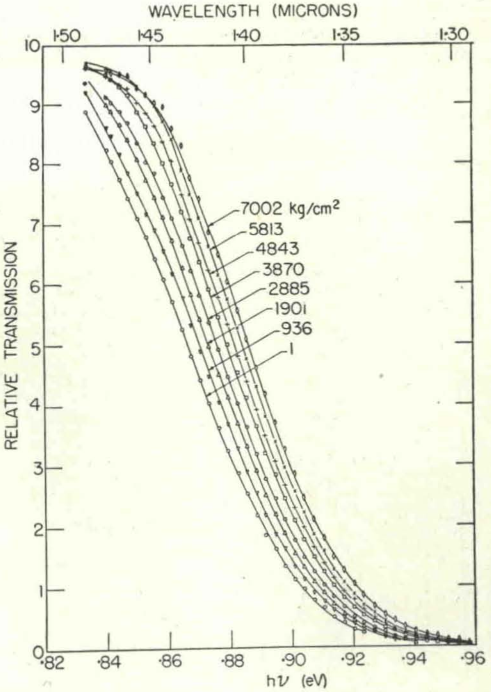
When a hydrostatic pressure sufficient to decrease the interatomic spacing by 0·1 per cent is applied to germanium, the energy gap increases by 0·01 eV, while in silicon the same compression decreases the gap by 0·004 eV. If the germanium interatomic distance is altered 0·1 per cent by alloying with silicon, a gap change of 0·03 eV is calculated in the germanium-rich region. At the silicon end a 0·1 per cent change in interatomic spacing *increases* the energy gap by 0·01 eV.

The interpretation of the position of the absorption edge as a function of composition is that the observed edge for any intermediate composition is a suitable average of the indirect transitions to both (100) and (111) minima. In like manner, the dependence of the pressure derivative of the forbidden gap depends on the relative importance of transitions to each minimum. Below the 15–20 per cent silicon range, the (111) minimum characteristic of germanium dominates the slope, while above this range the (100) behavior predominates.

A discrepancy will be noted in the data for the 3 per cent silicon sample. The long-wavelength transmission of the sample reached a maximum of only a few per cent. Consequently, we tend to reject the validity of the data from this sample. The results are presented for completeness, however, and to indicate that optical measurements on an alloy can be affected by the nature of the crystal. It is tempting to speculate that the discrepancies between the conclusions of LEVITAS *et al.*⁽⁵⁾ and JOHNSON and CHRISTIAN⁽⁴⁾ and those of later workers arise from some such effect as large fluctuations of one component. The possibilities have not been investigated to date.

(*Right*)

FIG. 9. Relative transmission of 11·5 per cent silicon in germanium alloy (RCA D106N) versus photon energy, at several pressures.



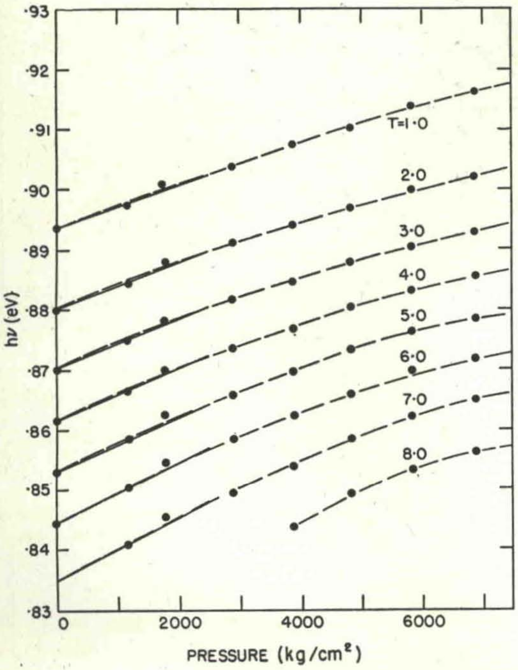
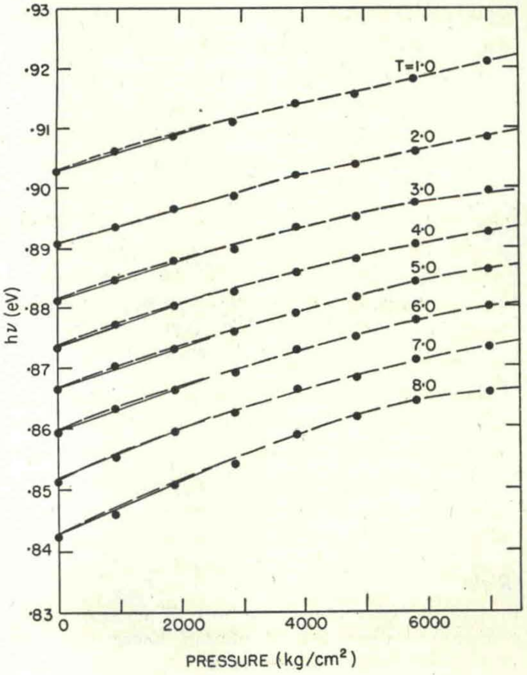


FIG. 8. Isotransmission plot of 11 per cent silicon in germanium alloy (RCA D106T). Average slope = $4{\cdot}42\times10^{-12}$ eV/dyne—cm^{-2}.

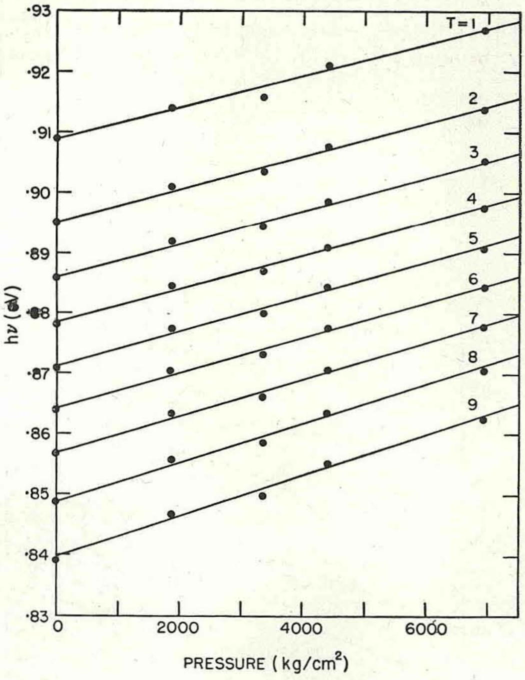
(*Right*)

FIG. 10. Isotransmission plot of 11·5 per cent silicon in germanium alloy (RCA D106N). Average slope = $3{\cdot}41\times10^{-12}$ eV/dyne—cm^{-2}.



(*Right*)

FIG. 12. Isotransmission plot of 12 per cent silicon in germanium alloy (RCA D102C). Average slope = $2{\cdot}97\times10^{-12}$ eV/dyne$-$cm^{-2}.



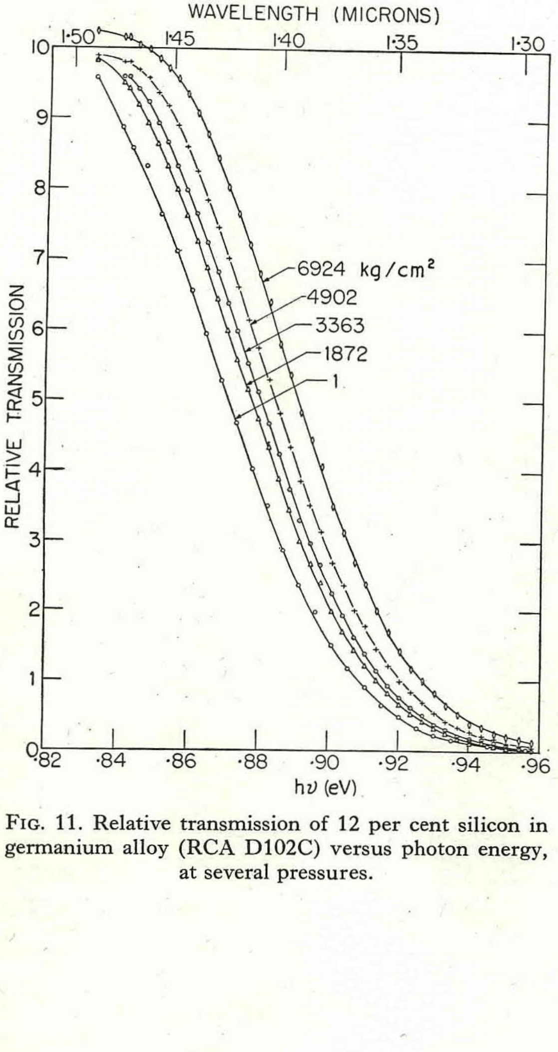
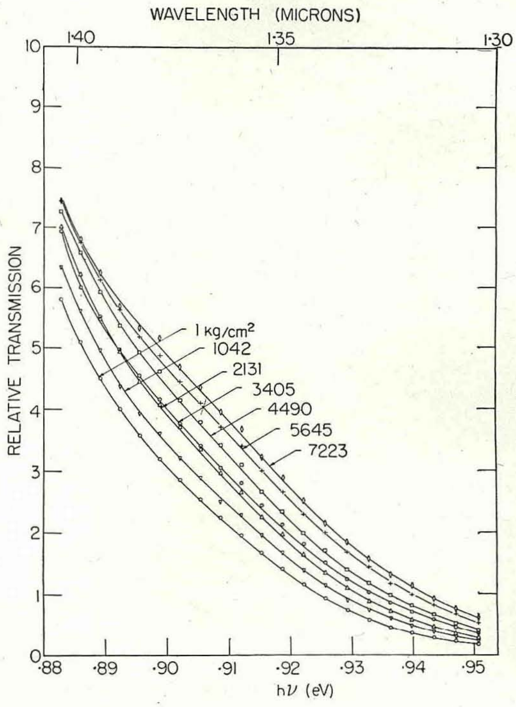


FIG. 11. Relative transmission of 12 per cent silicon in germanium alloy (RCA D102C) versus photon energy, at several pressures.

(*Right*)

FIG. 13. Relative transmission of 13 per cent silicon in germanium alloy versus photon energy, at several pressures.



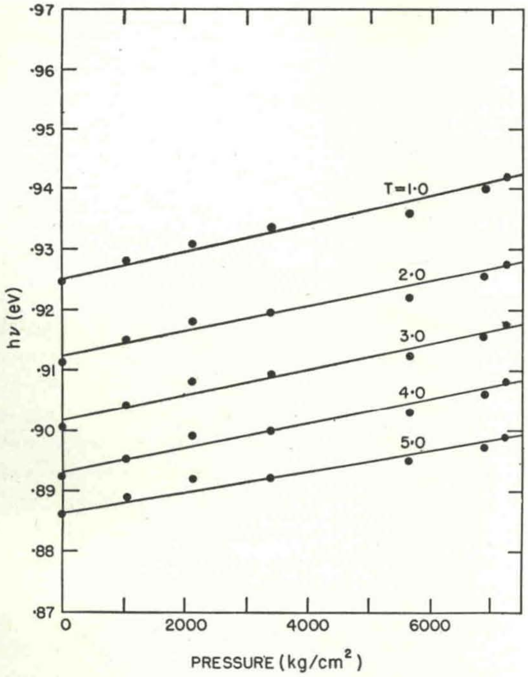


FIG. 14. Isotransmission plot of 13 per cent silicon in germanium alloy. Average slope = $2{\cdot}08\times10^{-12}$ eV/ dyne$-$cm^{-2}.

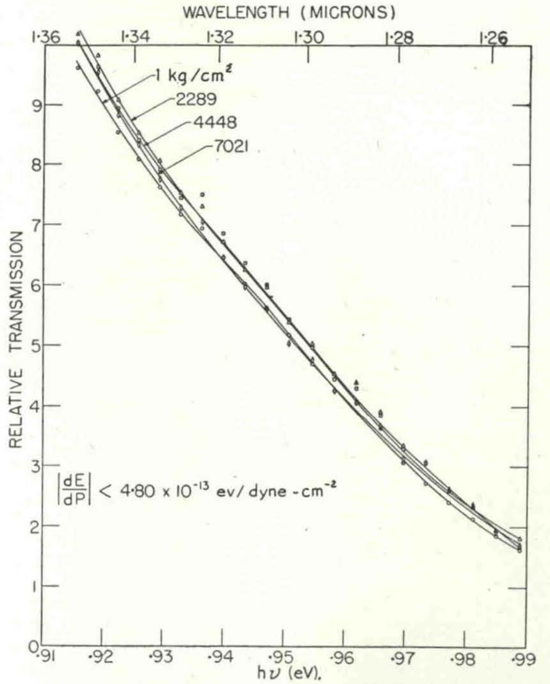


FIG. 15. Relative transmission of 18 per cent silicon in germanium alloy versus photon energy, at several pressures.

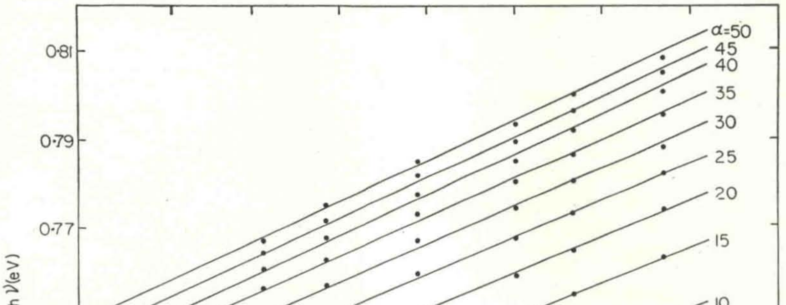


FIG. 16. Germanium isoabsorption data. See reference (1) for interpretation of slope.

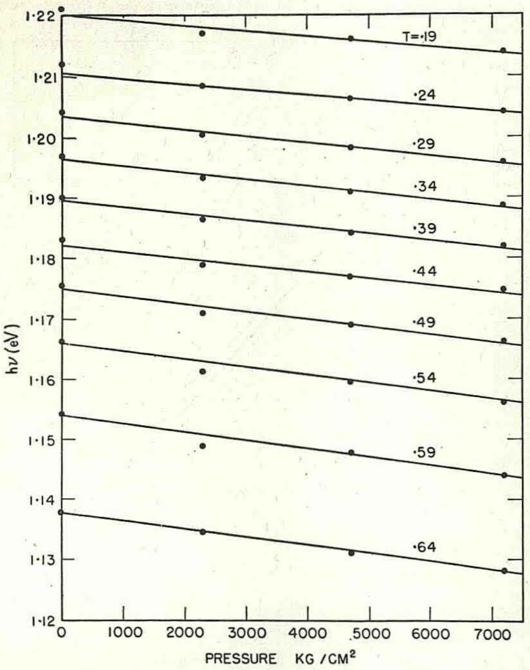


FIG. 17. Silicon isotransmission data. Average slope is $-1{\cdot}3\times10^{-12}$ eV/dyne$-$cm^{-2}.

Another problem arises in connection with the curvature of the isotransmission plots. A linear isotransmission plot implies a linear shift in energy of the edge with pressure, while parallelism of the curves indicates that no change is occurring in the shape of the edge.

The isotransmission curves for germanium are not parallel, whereas those for silicon are. The curves for intermediate compositions are approximately parallel. The non-parallelism in the case of germanium was ascribed to a change in the shape of the absorption edge with pressure, resulting from the change in separation of the (111)–(000) minima, which occurs as an energy denominator in the expression for indirect absorption. This separation is very large in silicon, so that changes in it would not be noticed. If this view is correct, only the alloys of low silicon content will show nonparallelism, and then only slightly. It is not advisable to check this with the isotransmission curve for the 3 per cent silicon sample for the reasons mentioned earlier. It is quite possible that, had a good 1–3 per cent silicon alloy sample been available, a shape change similar to that in germanium would have shown up.

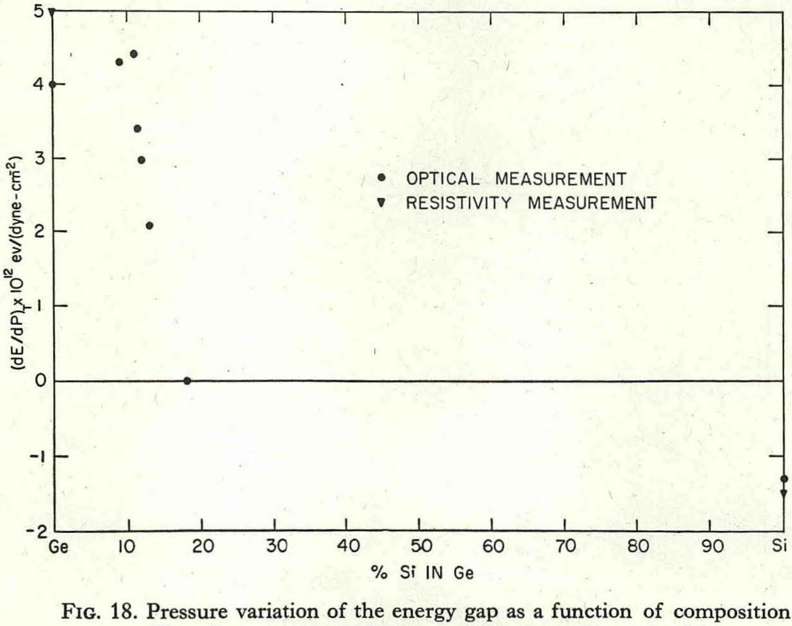


FIG. 18. Pressure variation of the energy gap as a function of composition. (Data for germanium–3 per cent silicon sample omitted.)

The isotransmission curves for silicon and germanium are linear, but those for the intermediate compositions are not all so. If the picture of the movement of the minima with pressure and alloying is correct, a bending over of the curves of $h\nu$ versus P would be expected at the high-pressure end for samples in which transitions into both types of minima decide the character of the absorption edge.

A definite trend towards quadratic behavior in our curves as a function of composition would therefore be understandable. The curves, however, seem to show curvature in a way which is not simply related to composition. On the other hand, our measurements of $h\nu$ and of pressure are quite accurate, and it is consequently difficult to ascribe this phenomenon to experimental error.

For the reasons given in the earlier papers, and also for the reasons just cited, no attempt was made to fit the data to a one-phonon process of indirect optical transitions. On the other hand, more recent experiments indicate the possibility that the indirect transitions can involve either of two phonons(11) for germanium, or any of four for silicon. However, as shown in our discussion of germanium, it is possible to fit the absorption to a one-phonon process without much difficulty. A two-phonon process supplies even more leeway in matching theory and experiment, unless some means is available to detect the effect of each phonon individually. Even if warranted, such detail would be lacking here because of our inability to secure a large optical aperture for high-resolution work in a high-pressure system, and secondly, because of the difficulties inherent in making high-pressure measurements over a wide temperature range. Thus, we do not attempt to fit our data with a two-phonon model.

In summary, measurements have been made of the change with pressure of the energy gap in germanium–silicon alloys. These measurements are consistent with the properties of germanium and silicon and with the behavior of their alloys as a function of composition reported by other workers.

Acknowledgements—We gratefully acknowledge the help of RCA Laboratories and Sylvania Products, Inc., in supplying us with alloy samples and data on them. The exchange of information with the personnel of RCA and especially with Dr. R. BRAUNSTEIN was appreciated. Professor HARVEY BROOKS, Mr. M. G. HOLLAND, Mr. MARSHALL I. NATHAN, and Mr. ARTHUR C. SMITH spent considerable time in discussing the results of this work. Again we wish to thank Professor P. W. BRIDGMAN for allowing us to use much of his high-pressure equipment.

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