Studies on Group III–V Intermetallic Compounds*†

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(Received July 26, 1957)

A study has been made of the properties of the compounds GaAs and InSb alloyed with Si, Ge, Sn, and Pb; the quasi-binary InSb–GaSb was also investigated. Lattice parameter, infrared absorption, and electrical resistivity measurements were made. The forbidden energy gaps of the GaAs alloys were found to vary inversely with the spacing, with the one exception of the GaAs–Ge alloy, where the reverse effect was observed. On the basis of the infrared transmission and electrical resistivity data it was concluded that the Group IV elements substituted for nearest-neighbor pairs in GaAs, but in the case of Si and Ge in InSb it appeared that the substitution of only one atom in the unit polyhedron occurred.

I. INTRODUCTION

SOME of the Group III–V compounds which crystallize in the zinc blende structure are semiconductors, and Welker[1] has shown that these compounds have many interesting properties. Only combinations of Group III elements with s^2 and p^1 outer electrons and Group V elements with s^2 and p^3 outer electrons would be expected to produce a semiconductor with tetravalent bonding. Of these combinations, the aluminum, gallium, and indium phosphides, arsenides, and antimonides have been found to be semiconductors, but the data on arsenides and phosphides are quite meager. The antimonides have been investigated in some detail, probably because they are the easiest to produce.

This work is concerned in part with the preparation and the properties of GaAs. In addition, the Group IV elements, Si, Ge, Sn, and Pb were added to GaAs to determine the solubility of these elements in the compound and to observe the influence of alloy additions on the interatomic distance, resistivity, and forbidden energy gap. Infrared absorption measurements were used to follow the changes in energy gap. Similar additions were also made to the compound InSb, and the quasi-binary InSb–GaSb was investigated in order to observe the effects of substituting one Group III element for another.

II. GaAs–GROUP IV ALLOYS

The compound, GaAs, was prepared from 99.95% pure Ga which was subsequently zone-refined and from 99.99% pure As. A mixture containing 55 atomic percent Ga was heated at 900°C in a sealed, evacuated double-walled quartz bomb. The compound was thus produced in a liquid matrix and the problems arising from excessive arsenic vapor pressure were thus alle-

viated. The resultant material was powdered and the excess Ga was removed by leaching in concentrated HCl. The compound could than be melted without danger of explosion since the vapor pressure of As over the compound at the melting point is approximately one atmosphere. The GaAs was zone refined vertically in a double-walled quartz tube by lowering the tube through a resistance furnace at 800°C, a narrow induction coil (5 Mc/sec), and a second resistance furnace in series. The resistance furnaces prevented condensation of As in equilibrium with the molten compound.

The GaAs alloys containing Group IV elements were made by melting the compound and the solute element in a sealed, evacuated, double-walled quartz tube, holding the mixture at the melting point for one-half hour and then pulling the tube out of the hot zone at a rate of about one inch per hour. This technique produced homogeneous alloys with a large grain size.

The solubilities of the Group IV elements were determined from lattice parameter measurements using CuK_α radiation and a 114.6-mm powder camera. Film-shrinkage corrections were made and additional errors[2] were minimized by extrapolating the apparent lattice parameters vs the function $\frac{1}{2}(\cos^2\theta/\theta + \cos^2\theta/\sin\theta)$, where θ = Bragg angle. The lattice-parameter data are summarized in Fig. 1, and Vegard's law was assumed to hold in determining the extent of solubility in each case. It is interesting to note that the solubilities of Si, Ge, Sn, and Pb in GaAs are all very similar, being between 0.50 and 0.60 atomic percent. In each case, however, there is an appreciable decrease in the lattice parameter of the arsenide on alloying, and the lattice parameter of the saturated compound appears to be remarkably constant.

The forbidden energy gap was measured for each of the compounds by determinations of infrared transmission using a Perkin-Elmer single beam, double-pass, infrared spectrometer. A silicon-carbide rod heated electrically to about 1100°C was used to provide a source of continuous radiation. The samples were thin disks, ground to 0.010 inch in thickness and polished metallographically on both sides. The thin sections were

[1] H. Welker, Z. Naturforsch. 7a, 744 (1952); 8a, 248 (1953).

[2] T. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) 57, 160 (1945).
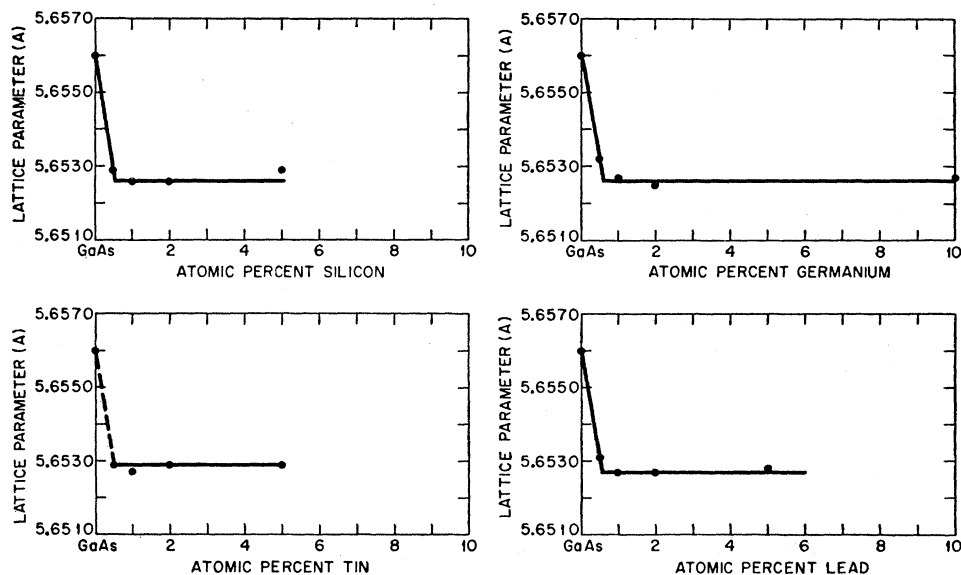
FIG. 1. Lattice parameters of GaAs alloys as a function of impurity content.

mounted on a brass holder so that the light completely covered the sample. A sodium chloride prism was used for all measurements because of its large infrared transmission range. A standard technique of comparing intensity *vs* wavelength with and without the sample in place was employed.

Figure 2 shows the effects of silicon additions on the infrared transmission properties of the arsenide. It is evident from Table I that the alloy containing 0.5 atomic percent silicon is a single-phase material; Fig. 2 indicates that the transmission edge for the alloy is at a slightly shorter wavelength than for the pure compound, and the forbidden energy gap has been correspondingly increased. It was found that all of the single-phase materials exhibited transmission curves which were quite parallel in the steep portion, and
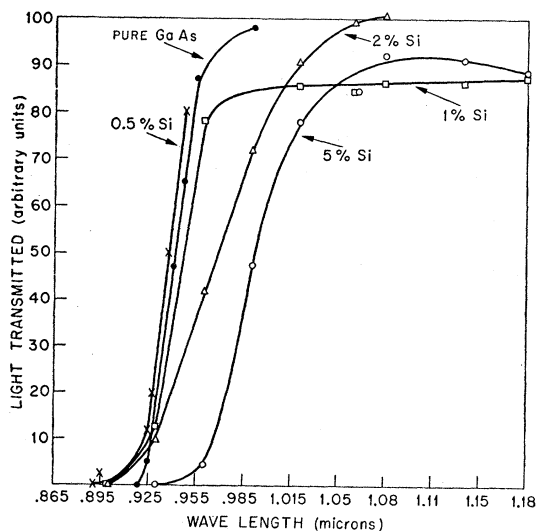

FIG. 2. Transmission curves for GaAs–Si alloys.

relative shifts of the absorption edges were expressed in terms of the wavelength at the half-power point. The GaAs–1% Si alloy, on the other hand, exhibited a half-power point at a longer wavelength, and it should be noted that this material contains two phases. A similar progression was noted for the 2 and 5% Si alloys. The transmission curves for the two-phase alloys represent a superposition of two transmission curves, one for GaAs saturated with Si and one for Si saturated with GaAs.

The resultant transmission curve for a material containing two phases A and B will depend upon the percentages of A and B present, the absorption coefficient of each phase at every wavelength, and the thickness of the sample. If a phase B has the lower energy gap and is added to A in small amounts, the resultant transmission curve will shift to longer wavelengths with a change in slope. If the sample being measured is too thick, a small amount of B can prevent the transmission of light until the transmission range of B is reached. If the difference in energy gaps is small, it is also possible to observe a transmission curve which has two plateaus. The observed shifts in the absorption curves to longer wavelengths and the changes in slope are thus consistent with the presence of two phases in these materials.

The effects of adding varying amounts of Ge to GaAs are shown in Fig. 3. Germanium was the only Group IV element which lowered the forbidden gap even when it was completely dissolved in GaAs. The effects of Ge addition beyond 0.5 atomic percent on the shape of the transmission curve are due to the presence of two phases in these alloys and the fact that germanium, with an energy gap of 0.71 ev, has a transmission range which occurs at much longer wavelengths than the transmission edge for GaAs.

TABLE I. Lattice parameters and energy gaps of GaAs–Group IV alloys.

Material (at. %)	Lattice parameter (A)	No. of phases	Half-power λ (microns)	ΔE_G[a] (ev)	$\left(\dfrac{\Delta E_G - \Delta E_G\ (\text{alloy})}{\Delta E_G}\right) \times 100$
GaAs	5.6560		0.942	1.320	
GaAs+ 0.5% Ge	5.6532	1	0.954	1.303	−1.29
+ 1% Ge	5.6527	2	0.963	1.291	−2.20
+ 2% Ge	5.6525	2	0.988	1.258	−4.70
+10% Ge	5.6527	2	very smeared	. . .	. . .
GaAs+ 0.5% Si	5.6529	1	0.938	1.325	+0.38
+ 1% Si	5.6526	2	0.945	1.315	−0.38
+ 2% Si	5.6526	2	0.969	1.283	−2.80
+ 5% Si	5.6529	2	0.990	1.256	−4.85
GaAs+ 0.5% Sn	5.6529	1	0.928	1.339	+1.44
+ 1% Sn	5.6527	2	0.926	1.342	+1.67
+ 2% Sn	5.6529	2	0.926	1.342	+1.67
+ 5% Sn	5.6530	2	brittle	. . .	. . .
GaAs+ 0.5% Pb	5.6531	1	0.937	1.327	+0.38
+ 1% Pb	5.6527	2	0.933	1.332	+0.91
+ 2% Pb	5.6527	2	0.933	1.332	+0.91
+ 5% Pb	5.6528	2	. . .	. . .	. . .

[a] Energy-gap measurements of two-phase alloys represent superposition of transmission curves for two semiconducting materials.

Figure 4 shows the transmission characteristics of GaAs containing Sn and Pb additions. The addition of each of these elements has produced an increase in the forbidden energy gap. The addition of Sn, which has a smaller atomic size, appears to have produced a larger relative shift in the energy gap than that produced by Pb. The two-phase alloys of GaAs–1% Sn and GaAs–1% Pb represent a different case for analysis than the two-phase Si and Ge alloys. In this instance, neither tin nor lead are semiconductors at room temperature. The presence of an excess of either element will not, therefore, cause a shift in the transmission curve of the semiconducting material, but will add free carriers to the compound. The presence of excess free carriers merely reduces the amount of light transmitted. Hence, the curves for the 1% Sn and 1% Pb alloys

must represent the transmission properties of GaAs saturated with these elements. That this is true is shown by the fact that the transmission curves for the 2% Sn and 2% Pb alloys coincide with the curves for the respective 1% alloys. It should also be noted that the infrared transmission properties represent a new method of determining the solid solubility limits of some metallic solutes in a semiconductor.
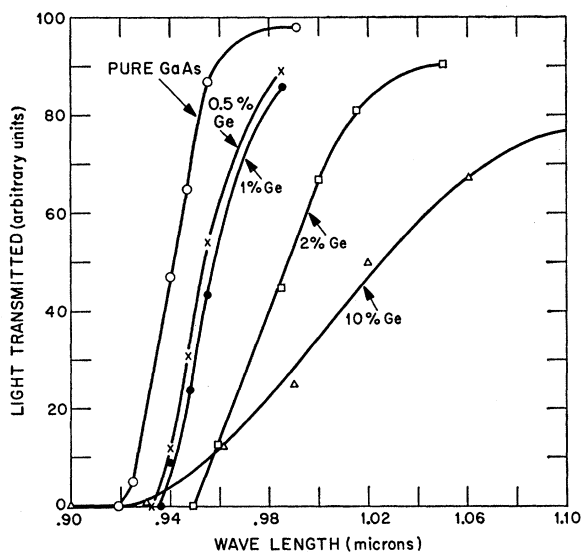

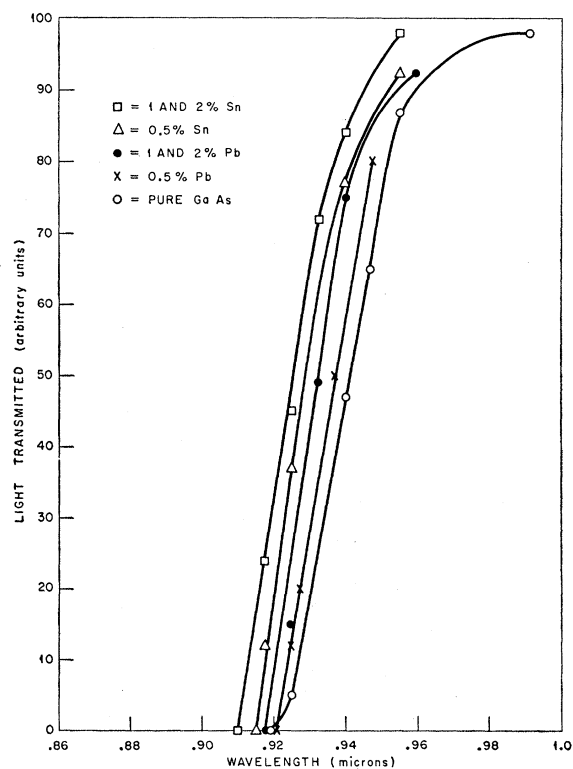FIG. 3. Transmission curves for GaAs–Ge alloys.

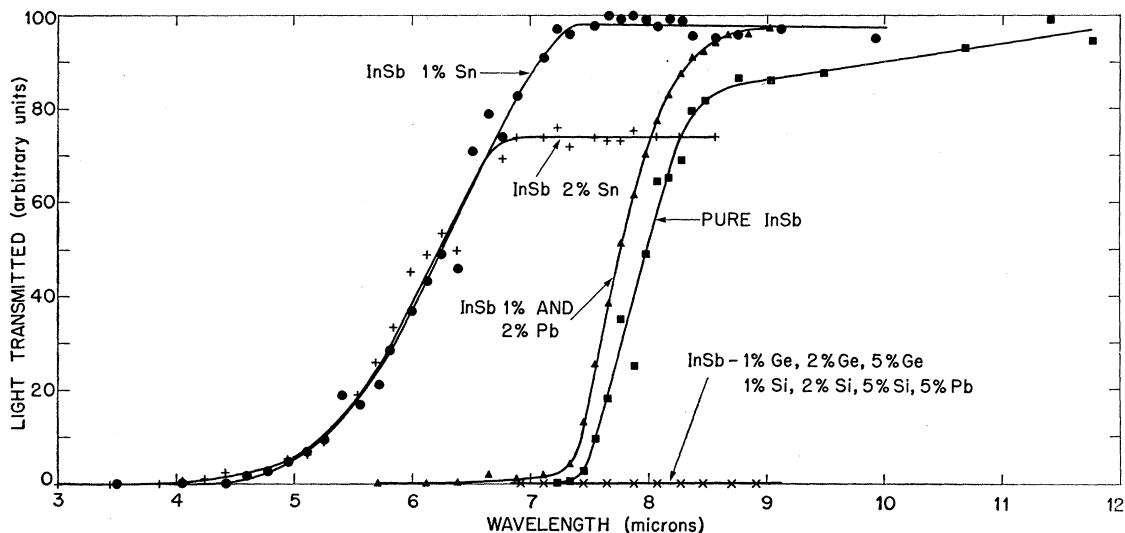FIG. 4. Transmission curves for GaAs–Sn and Pb alloys.

FIG. 5. Transmission curves for InSb–Group IV alloys.

The data for the GaAs–Group IV alloys are summarized in Table I which lists the wavelength at half-power, the corresponding energy gap, the lattice parameter, and the relative change in the forbidden energy gap for each alloy.

III. InSb–GROUP IV ALLOYS

InSb and GaSb were made by melting the zone-refined components in a smoked quartz boat under a hydrogen atmosphere. The compound was then further purified by zone melting. The InSb alloys were melted using induction heating to insure good mixing.

The infrared transmission properties of the InSb–Group IV alloys are shown in Fig. 5. As shown in Table II, all of these measurements were made on two-phase materials. Since the presence of a tin- or lead-rich phase does not affect the measurement of the forbidden energy gap of InSb saturated with these elements, the optical transmission properties of the solid solutions could be determined. An excess of either germanium or silicon, on the other hand, could shift the transmission

curves of InSb saturated with either of these elements to shorter wavelengths since they both have forbidden energy gaps greater than that of InSb. However, it was found that the presence of silicon and germanium in InSb completely prevents any transmission over the wavelength span investigated, as shown in Fig. 5. It is possible that silicon and germanium substitute preferentially for only one of the atoms in the InSb lattice.[3] This type of substitution would contribute excess carriers which in turn would absorb energy from the incident light and thus render the alloy opaque.

The addition of lead to InSb is seen to increase the energy gap (half-power values) from 0.157 ev to 0.161 with a decrease in the lattice parameter from 6.4867 A to 6.4800 A. The effect of adding tin to InSb is seen to be analogous to the effect of adding lead. In this case the forbidden energy gap has increased to 0.200 ev; however, the decrease in lattice parameter was the same as for the InSb–Pb alloys. Thus, the smaller Sn atom has caused a greater increase in the energy gap than the larger Pb atom, although the equivalent alloys have equal lattice spacings.

TABLE II. Lattice parameters and energy gaps of
InSb–Group IV alloys.

Material (at. %)	Lattice parameter (A)	No. of Phases	Half-power λ (microns)	ΔE_G (ev)
InSb	6.4867	1	7.92	0.157
InSb+ 1% Si	6.4790	2	opaque	...
+ 2% Si	6.4788	2	opaque	...
+ 5% Si	6.4790	2	opaque	...
+10% Si	6.4788	2	opaque	...
InSb+ 1% Ge	6.4788	2	opaque	...
+ 2% Ge	6.4788	2	opaque	...
+ 5% Ge	6.5790	2	opaque	...
InSb+ 1% Sn	6.4800	2	6.22	0.200
+ 2% Sn	6.4797	2	6.22	0.200
InSb+ 1% Pb	6.4790	2	7.72	0.161
+ 2% Pb	6.4800	2	7.72	0.161

TABLE III. Lattice parameters and energy gaps of
GaSb–InSb alloys.

Material (at. %)	No. of Phases	Lattice parameter (A)	Half-power λ (microns)	ΔE_G (ev)
GaSb	1	6.0954	1.75	0.710
90 GaSb–10 InSb	1	6.1013	2.244	0.554
85 GaSb–15 InSb	2	6.1170		
70 GaSb–30 InSb	2	6.1195		
50 GaSb–50 InSb	2	...		
30 GaSb–70 InSb	2	6.4788		
15 GaSb–85 InSb	2	6.4788		
10 GaSb–90 InSb	2	6.4787		
InSb	1	6.4867	7.92	0.157

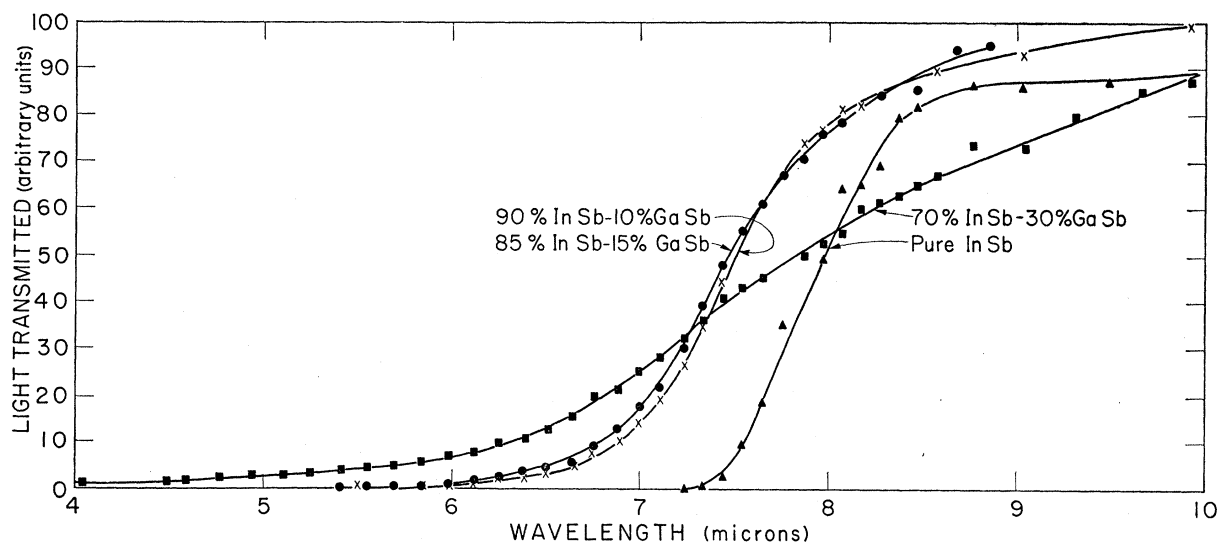[3] E. Schillman, Z. Naturforsch. 11a, 463 (1956).

FIG. 6. Transmission curves for InSb–GaSb alloys.

IV. InSb–GaSb ALLOYS

In order to determine the extent of substitution of indium and gallium in the corresponding antimonide compounds, nine alloys including the pure compounds were made. Figures 6 and 7 show the optical transmission properties of these alloys. The corresponding lattice spacings and energy gaps are given in Table III. It appears that the solid solubility of InSb in GaSb lies between ten and fifteen atomic percent and that of GaSb in InSb is less than ten percent. Thus, the transmission curves shown in Fig. 6 represent the transmission properties of two-phase materials. However, the addition of GaSb to InSb is seen to have increased the energy gap of InSb. This is indicated by the fact that the curve of the 90% InSb–10% GaSb alloys is at a shorter wavelength and lies closely parallel to the curve

of pure InSb. Energy gaps cannot be determined from these curves, however, since they represent the sum of two transmission curves.

Figure 7 shows the transmission curves for the high percentage GaSb alloys. Several additional effects can be seen in the case of the high GaSb alloys. The addition of 10% InSb to GaSb has decreased the forbidden gap from 0.71 ev to 0.55 ev. It is evident that the single-phase 90% GaSb–10% InSb alloy has a transmission curve with the same shape as that of GaSb. The curves in Fig. 7 of the two-phase alloys have completely different properties, however, in that a double transition is observed for each of these materials. Since the separation of the absorption edges is large for the saturated solid solutions, the double transition cannot be a result of adding their individual transmission curves. This is
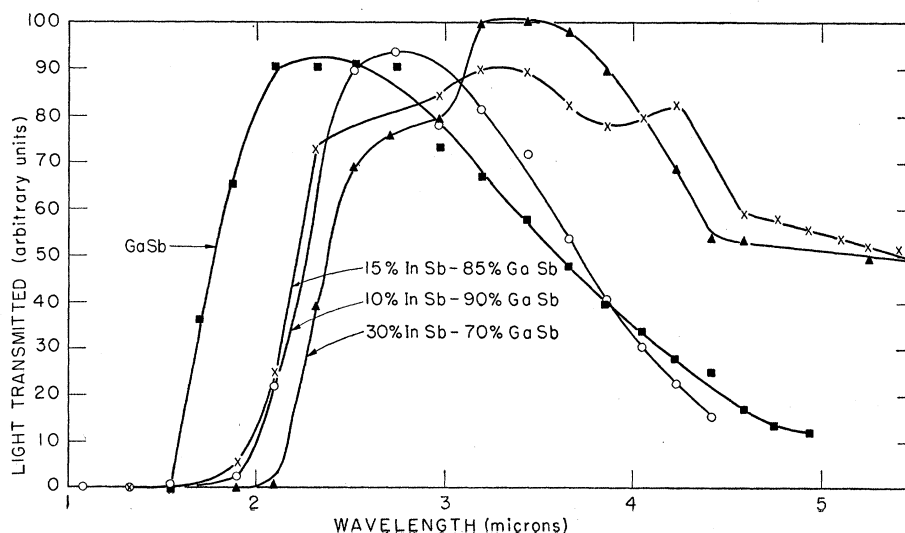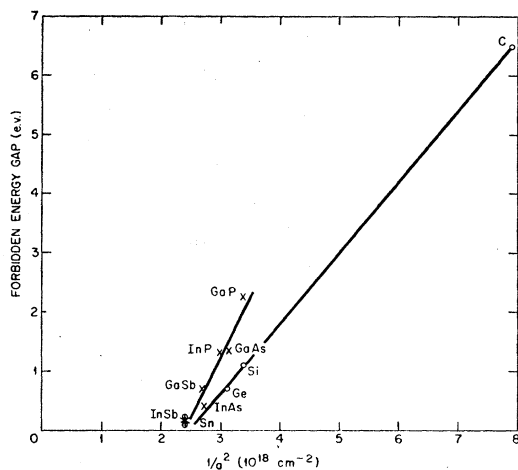

FIG. 7. Transmission curves for GaSb–InSb alloys.

FIG. 8. Energy gaps of tetravalent semiconductors as a
function of $1/a^2$.

evidenced by the curve for 85% GaSb–15% InSb. This
curve shows a transition at a slightly higher energy
level than that of the single-phase 90% GaSb–10% InSb
alloy and another very smeared transition at a longer
wavelength. Thus, the further exchange of indium for
gallium has probably resulted in a further shift in the
relationship between two minima in the conduction
band. The exact shift between the minima cannot be
determined because the effect of the second InSb-rich
phase is to displace the whole curve to the right. Thus,
the curve of GaSb saturated with InSb would have a
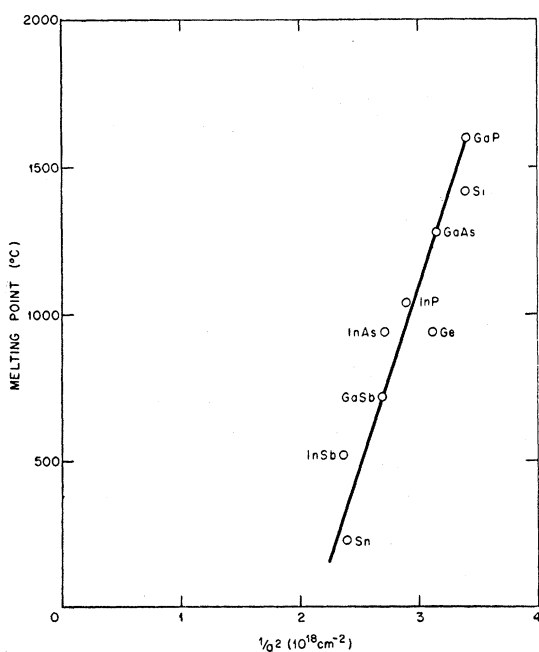similar shape and would lie further to the left than that

FIG. 9. Melting points of tetravalent semiconductors as a
function of $1/a^2$.

of the 85% GaSb–15% InSb. It appears that a higher
minima has been lowered since one of the transitions
lies to the left of the transition for the 90% GaSb–
10% InSb alloy. Unfortunately, the exact position of
this transition is not determinable. Similarly, the curve
for 70% GaSb–30% InSb lies farther to the right than
the 85% GaSb–15% InSb curve due to the presence of
the InSb-rich phase. In the two-phase alloys, the second
transition, or that lying furthest to the right in Fig. 7,
probably corresponds to the transition initially ob-
served in GaSb but now lowered in energy by the pres-
ence of indium in solid solution.

V. DISCUSSION

Pauling[4] has suggested that the covalent-bond energy
between two equally shared electrons at the minimum
bond distance is related to the reciprocal of the bond
length. This suggests that the forbidden energy gaps
of the Group IV semiconductors should exhibit a
similar relationship. The data in Fig. 8 indicate that
the energy gaps are proportional to $1/a^2$, where a is the
lattice parameter, and that a similar relationship holds
for the III–V intermetallic compounds. Figure 9 indi-
cates that the melting points also vary as $1/a^2$. The data
are probably not accurate enough to justify a choice
between an a^{-1} or an a^{-2} variation, but it is apparent
that the energy gap increases as the lattice parameter
decreases for these semiconductors.

In general, it was found that the energy gaps of the
Group III–V compounds increased on Group IV alloy
additions, consistent with the observed decreases in the
lattice parameters. The only exception arose in the case
of Ge additions to GaAs, and Table I shows that the
energy gap of GaAs–0.5 atomic percent Ge was lower
than for pure GaAs even though the lattice parameter
of the alloy was considerably smaller. Figure 10 shows
the observed variation of energy gap as a function of
$1/a$ for the GaAs–Group IV alloys. This relationship
appeared to give a better fit in the case of the Sn and
Pb alloys than a similar plot vs $1/a^2$, although the extent
of the data probably does not warrant a detailed ex-
amination on this basis. The energy-gap data for two-
phase alloys of Sn and Pb are shown in Fig. 10 since a

TABLE IV. Resistivities of GaAs–Group IV alloys.

Material (at. %)	Resistivity (ohm-cm)
GaAs	0.001–0.006
	average 0.003
GaAs+0.5% Si	0.0019
+1% Si	0.002
GaAs+0.5% Ge	0.12
+1% Ge	0.007
GaAs+0.5% Sn	0.0019
+1% Sn	0.023
GaAs+0.5% Pb	0.0025

[4] L. Pauling, J. Phys. Chem. 58, 662 (1954).

small quantity of metallic phase does not interfere with the transmission measurement.

Since GaAs has a zinc blende structure, it would seem that additions of Group IV elements should maintain both the tetravalent bonding and the electron stoichiometry. This can only be accomplished, however, if the solute atoms enter the GaAs lattice in pairs, replacing two neighboring unlike atoms. On the basis of electrical resistivity and Hall measurements, Schillman[3] decided that Group IV elements enter the compound InAs with a replacement of In atoms only. Each Group IV atom would thus act as a donor and contribute an electron to the lattice. With the relatively large solubilities found in the case of the GaAs–Group IV alloys a similar substitution would produce a large decrease in electrical resistivity. Although such changes were observed by Schillman in the case of InAs, the resistivities of the GaAs alloys, which are listed in Table IV, remained essentially constant in these experiments. In the case of GaAs it thus appears that the solute atoms substitute for Ga and As atoms in pairs.

The preferential type of replacement appears to occur in InSb as evidenced by the opaqueness of these alloys to infrared light and the change in resistivity of the InSb upon alloying as shown in Table V. A similar opaqueness was not observed in the case of the corresponding GaAs alloys, and it was concluded that the Group IV elements substituted for the Ga and As atoms in nearest-neighbor pairs. This difference in behavior between the arsenide and the antimonide may be associated with the sizeable difference in the respective lattice parameters. Both Si (5.4282 A) and Ge (5.658 A) are quite similar in lattice size to GaAs (5.6560 A). A substitution of Si or Ge for either of the elements in the compound would be possible, but a substitution for a nearest-neighbor pair would result in a lower total energy by avoiding the formation of a new electron energy level associated with an unpaired electron. On the other hand, InSb (6.4867 A) has a much larger lattice, and the substitution of a pair of very small atoms seems unlikely because of the large local distortion produced. It thus appears that in the latter case the substitution of only one atom occurs in a unit tetrahedron with the consequent formation of a new local energy level. The sizes of the Sn and Pb lattices on the other hand, are much closer to that of the

TABLE V. Resistivities of InSb–Group IV alloys.[a]

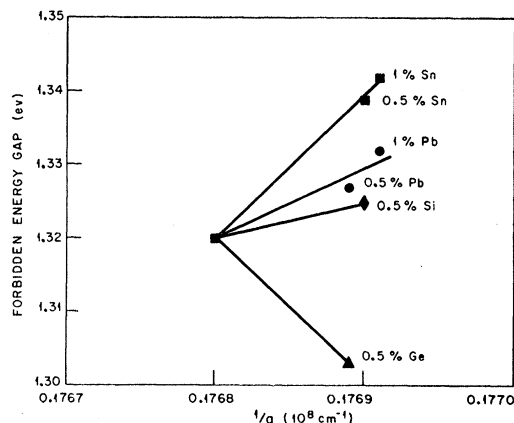| Material (at. %)	Resistivity (ohm-cm)
InSb	0.905
InSb+0.5% Si	0.057
+0.5% Ge	0.005
+0.5% Sn	0.0005
+0.5% Pb	0.0355

[a] 77°K.

FIG. 10. Forbidden energy gap vs $1/a$ for GaAs alloys.

antimonide and some pairwise substitution could occur. This was apparently observed since Table II shows that these alloys exhibited some infrared transmission.

Additions of Group IV elements to high-purity[5] InSb have been shown to decrease the lattice parameter and to increase the forbidden energy gap. These energy-gap changes cannot be attributed to degeneracy[6] since a decrease in transmitted intensity was not observed at long wavelengths as in all of the degenerate samples studied by Tanenbaum and Briggs.[7] Zitter[8] has reported that the forbidden energy gap of InSb was insensitive to the presence of Sn, but this material was very impure[9] and the effect of the Sn additions was probably masked.

It is interesting to observe that Folberth[10] found a complete series of solid solutions in the system GaAs–GaP and Weiss[11] observed a similar situation in the InAs–InP system. In this work the solubility limits of the GaSb–InSb system were found to be only about 10%, whereas Woolley, Smith, and Lees[12] report complete solid solubility after prolonged annealing. The GaInSb$_2$ alloy of Blakemore[13] was two-phase material, however, leaving some doubt as to the equilibrium compositions of the GaSb–InSb alloys.

ACKNOWLEDGMENTS

[5] p type, 5×10^{14} carriers/cc at 77°K.
[6] E. Burstein, Phys. Rev. **94**, 1431 (1954).
[7] M. Tanenbaum and H. Briggs, Phys. Rev. **91**, 1561 (1953).
[8] R. N. Zitter, Chicago Midway Laboratories (private communication).
[9] 99.9% pure In and 99.9% pure Sb.
[10] D. G. Folberth, Z. Naturforsch. **10a**, 502 (1955).
[11] H. Weiss, Z. Naturforsch. **11a**, 430 (1956).
[12] Woolley, Smith, and Lees, Proc. Phys. Soc. (London) **B69**, 1339 (1956).
[13] J. S. Blakemore, Can. J. Phys. **35**, 91 (1957).