

PREPARATION OF III-V ALLOYS, AND
ELECTRICAL TRANSPORT UNDER
HYDROSTATIC PRESSURE

by

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ORIGINALITY

The following aspects of this thesis represent original work performed by the author during graduate studies at the University of Ottawa.

(1) Extension of imperfect mixing theory in dilute solutions to the more general case of alloys.

(2) Computer studies of the variation of alloy composition along ingots.

(3) Concept and introduction of an original technique (sequential growth) for preparing highly-segregating alloys in the form of ingots having gradually-tapered composition.

(4) Preparation of $\text{InAs}_x\text{Sb}_{1-x}$, $\text{GaAs}_x\text{Sb}_{1-x}$ and $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ of improved quality by sequential growth.

(5) Identification of high-resistance barriers at grain boundaries in Te-doped, GaSb-rich alloys as the principal reason for erratic apparent mobilities in prior work.

(6) Measurements of resistivity and Hall coefficient under hydrostatic pressures up to 12 kilobars (Kb), especially on the above alloy systems.

(7) Improved analysis of pressure results, involving detailed assessment of electron scattering in the $\langle 000 \rangle$ conduction band*, and leading to the determination of the energy separation between the $\langle 000 \rangle$ and $\langle 111 \rangle$ minima in alloys containing GaSb.

* see Acknowledgments.

(8) Experimental evidence against the belief that the $\langle 111 \rangle$ conduction band is populated by electrons in heavily-doped InAs*.

* see Acknowledgments.

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The advice and encouragement of Professor J.C. Woolley has been of great value during the course of this project, including the preparation of this thesis, and the stimulating atmosphere provided by his students and colleagues has also been a great asset.

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Thanks are also due to Messrs. J. Basinski, R. Senechal and A. Taylor, who respectively prepared the Te-doped GaSb, heavily - Se-doped InAs, and $\text{InAs}_{0.96}\text{Sb}_{0.04}$ used in three of the pressure experiments.

Cooperation with Dr. Basinski was also an important factor in the analysis of electron scattering in GaSb and its alloys.

This thesis has been typed by Diane Perron.

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1. INTRODUCTION

Prior to this project, three of the four ternary alloy systems that occur among the compounds GaAs, InAs, GaSb and InSb had been extensively examined, in this laboratory or elsewhere. These were $\text{Ga}_x\text{In}_{1-x}\text{As}$, $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ and $\text{InAs}_x\text{Sb}_{1-x}$. The fourth system, $\text{GaAs}_x\text{Sb}_{1-x}$ had been less investigated, due to difficulties involved in its preparation. Similar but less severe difficulties in the preparation of $\text{InAs}_x\text{Sb}_{1-x}$ had been overcome by Coderre (69C3) and others, except that the step-freeze method used in most of the successful preparations furnished ingots having steep composition gradients in the range $0.3 \leq x \leq 0.75$, and also some inhomogeneity in the range $0.5 \leq x \leq 0.7$.

Alloy preparation work was undertaken principally with a view to furnishing specimens of the latter two systems at all compositions. As will be seen, this objective later shifted as attention was drawn especially towards alloys rich in GaSb. For this reason, no attempts were made to prepare $\text{GaAs}_x\text{Sb}_{1-x}$ in the range $x \geq 0.45$, and the highest composition actually attained was 0.36. Progress was made in understanding of alloy growth, and on the practical side, ingots having smoothly-tapered composition profiles were prepared, which provided more abundant specimens for measurements.

Progress was also made in the growth of n-type, GaSb-rich alloys by Te-doping, the original intention being merely to provide samples for pressure work at room temperature. Previous resistivity measurements

in this laboratory on Te-doped $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ had not given consistent results at room temperature, and characteristic mobilities were deduced by extrapolation from high temperatures (69C4). The cause of this problem, namely the resistance barriers described here, had not then been recognized. On the other hand, the carrier densities determined by room temperature Hall effect, and used in the analysis of optical data in this laboratory, are not invalidated; as will be seen, the Hall effect is not seriously upset by the barriers. By the use of zone growth, the crystalline quality was improved, and this aided the selection of specimens which were practically free from barriers. Equivalent results were obtained when Te-doping was introduced into the growth of $\text{GaAs}_x\text{Sb}_{1-x}$.

Apparatus for the measurement of Hall effect and resistivity under hydrostatic pressure was set up, to provide an alternative to the use of temperature as a variable. For technical reasons, the pressure measurements were made at room temperature, and this limited the kind of work that could be done. The pressure variation of the main band-gap could not be studied, except in materials having appreciable intrinsic conduction. The study of transport in p-type materials tends to be unrewarding, since pressure has little effect on the valence bands. In single-band n-type materials such as the alloys of InAs, the variation of mobility with pressure is of interest, and some work was started in this area, but the main effort was directed to n-type, GaSb-rich alloys, which show 2-band conduction and complex mobility variations in the pressure range up to 12 Kb.

The most fundamental parameter governing the pressure behaviour

in such alloys is the energy separation of the $\langle 000 \rangle$ and $\langle 111 \rangle$ conduction bands; therefore the determination of this band separation parameter at different compositions was a principal object of the pressure measurements. The pressure coefficients of this parameter were also of interest, although it was not expected that these would be very different from those of the unalloyed compounds.

Other measurements being performed (by others) in this laboratory included magneto-resistance, thermo-electric effects in magnetic fields, optical measurements on free carriers using reflectance and Faraday rotation, and measurement of optical transitions using modulated reflectance by several methods.

2. PREPARATION OF III-V ALLOYS

2.1 TECHNIQUES

Growth Techniques

A review of earlier work, including evidence for solid solution over whole composition ranges, and phase diagram determinations, has been given by Woolley (62W1). It was found relatively easy to prepare alloys among the compounds GaP, GaAs, InP, InAs, apart from the inherent difficulties in preparing the compounds themselves. New difficulties arose from attempts to prepare alloys between any of these four compounds and GaSb or InSb, due to the extreme segregation of components, associated with the wide separation of the liquidus and solidus curves on the phase diagram. Considerable progress has been made since then at many research centres, especially in liquid-phase and vapour-phase epitaxial growth, and in growth from non-stoichiometric liquids, of both epitaxial layers and bulk ingots. Aspects of this work will be introduced at suitable points.

Despite the value of such methods, the growth of ingots from stoichiometric liquids can be preferable for the growth of research specimens. In this laboratory, ingots were usually grown by one of three methods, viz. gradient freezing, step-freezing, and zone growth, all using stoichiometric liquids. In gradient freezing, the furnace has a thermal gradient of perhaps 5° to 10° over the length of the containing ampoule, the temperature being set high enough initially to form a

homogeneous liquid, then it is programmed down very slowly, so that freezing progresses from one end. The actual growth rate for high-segregation compositions is far slower than the nominal rate set by the programme controller, due to the fall of freezing temperature with composition. Inhomogeneous growth is a serious problem in gradient freezing, and the reasons for this are discussed in Section 2.2. Step freezing uses a furnace with broad hot and cool zones, separated by as short a distance as possible. Growth occurs as the ampoule is drawn mechanically from the hot zone into the cool zone, and homogeneous growth may be obtained at rates which are many times faster than in gradient freezing, but in both methods the resulting ingots (in the case of highly-segregating components) have very undesirable composition profiles, including a steeply-graded portion which cannot be eliminated by any choice of starting composition, if central compositions are to be achieved at all.

Zone growth requires the preparation of a starting ingot by some method, such as chill-casting a stoichiometric melt. The ingot is then drawn through a furnace consisting of two cool regions surrounding a short hot region, set at a high enough temperature to initiate and maintain a liquid zone within it. Provided only a small (but not too small) fraction of the ingot is liquid at anytime, the composition profile of the resulting ingot resembles that of the starting ingot, but with local inhomogeneities smoothed out. This "levelling process" ceases when the liquid zone reaches the end of the starting ingot, so the composition profile of the "end zone" region corresponds to a step-freeze.

In order to initiate the liquid zone the heater must be capable of raising the ingot tip to above its liquidus temperature; also, initial segregation results in a non-uniform composition over the first one or two zone lengths. Therefore, the liquid zone should be initiated in a plug of low-melting composition, which also would suppress the initial transient in the composition profile if the length of the plug were properly chosen. Kudman et al (67K2), (68K2) have used this procedure, choosing the compositions of the plug and main charge to have a liquidus: solidus relationship. Equivalent suppression of the initial transient could be obtained by using a plug of unalloyed compound and slightly shorter length, so that dissolution of the main charge would commence before the first freezing took place. This "plug" technique was not used in the present work, since an original concept (sequential growth) was introduced as an improvement. Zone growth seems to be preferable to various more elaborate techniques. Step-levelling for example, as reported by Dismukes et al (65D1), resembles a step-freeze but with the liquid region in contact with a dissolving solid charge inside the hot zone, which should have a uniform, closely-controlled temperature. In zone growth, the liquid-solid interfaces should be at points of maximum temperature gradient, which minimizes the need for accurate temperature control.

In all these methods, the cool zone(s) must be maintained at a sufficient temperature to prevent condensation of any volatile constituent (e.g. As) at a vapour pressure determined by the temperature of the hot zone, but must not exceed the solidus temperature for any part of the grown ingot.

Thin layers of various alloys have been prepared by liquid-phase epitaxial growth, (69S1), (70A1); in the case of $\text{GaAs}_x\text{Sb}_{1-x}$ the central compositions were not achieved, but Clough and Tietjen (69C2) reported success using vapour-phase deposition, the layers being only a few microns thick, and in a state of strain due to lattice mismatch with the semi-insulating GaAs substrates.

Bolvanovich (66B1) has reported the preparation of $\text{InAs}_x\text{Sb}_{1-x}$ from quenched melts, homogenized by heating for several days at temperatures above the solidus of the lower-melting phases. X-ray diffraction indicated a single phase in each specimen, of homogeneity from $\pm 2.5\%$ near the ends of the composition range, to $\pm 7.5\%$ near the centre. The materials reported by Coderre and Woolley (68C1), prepared by slow step-freezing, and those reported here, prepared by sequential growth, clearly resolve the K_α copper doublet at most compositions; within the range $0.4 \leq x \leq 0.6$ the doublet lines merge, corresponding to homogeneity of $\pm 1.5\%$. Sirota and Matyas (68S1) reported results in $\text{GaAs}_x\text{Sb}_{1-x}$ similar to those of Bolvanovich as mentioned above, but no information on line widths was given.

Sequential Growth

For research purposes a tapered composition is usually preferable since this reduces the number of ingots required to cover a range of compositions. The concept of sequential growth, which provided a practical means of achieving tapered profiles, arose from the following considerations. It was well known that the effective value of the segregation coefficient describing the composition of a solid freezing

out from a melt was in general dependent on both the degree of stirring and the growth rate. This has led to useful techniques, as for example the preparation of p-n junctions by growth rate variations, as described by Hall (52H1).

It therefore seemed probable that the very high segregation found in III-V alloys could be moderated by increasing the growth rate considerably, so as to complete the step-freeze in a time which was intermediate between the few seconds needed for chill-casting and the many weeks required for homogeneous growth. A step-freeze ingot grown rapidly in this way would not be homogeneous, but the average composition should be more gradually tapered than those prepared by slow growth. It also seemed clear that homogeneity could be achieved without destroying the tapered profile, by passing a short liquid zone very slowly through the ingot. The term "zone levelling" would be misleading and should not be used in this case, where a better name would be "zone averaging". By initiating the zone at the low-melting (i.e. last-to-freeze) end of the step-freeze ingot the advantage of the "plug" technique in not demanding a high initiation temperature could be combined with a simplified procedure, since the entire procedure could be conducted without opening the original ampoule in which the alloy was synthesised from its constituent elements. Further, improvement in the perfection of the averaging could be obtained by making a second zone pass in the reverse direction, which would also move the low-melting end-zone region back to the original low-melting end, thus restoring the composition profile to a monotonically-tapered shape.

Theoretical analysis and computer simulation of sequential growth were conducted, as described in Section 2.2. Comparisons with prior experimental work are also made in this section. In Section 2.3 the theoretical studies are related to the experimental data accumulated by the author in the extensive application of the sequential growth concept to the preparation of $\text{InAs}_x\text{Sb}_{1-x}$, $\text{GaAs}_x\text{Sb}_{1-x}$ and $\text{GaIn}_x\text{Sb}_{1-x}$.

In the latter alloy system a gradual tapering of composition is provided by step-freezing alone, but a subsequent zone pass was found to yield larger crystallite sizes, comparable to the cross-sectional dimensions, and indicating that single crystals might be obtained by use of a seed crystal. However, for this purpose the conventional zone levelling procedure as reported by Plaskett (69P2) should be preferable, since it is harder to optimize the shape and position of the freezing interface when the freezing temperature changes with time. Also, even a gradual composition taper must introduce some strain and dislocations due to lattice mismatch.

In the sequential growth of $\text{GaIn}_x\text{Sb}_{1-x}$ a further innovation was made in one instance, in that the single zone pass was initiated at the high-melting end of the step-freeze ingot. As can be readily explained from the phase diagram of this system, all compositions were in this way provided in a single ingot. Unfortunately this reverse-sequential growth was tried on a step-freeze ingot of rather unsuitable composition which happened to be available; there is little doubt that a starting composition $X = 0.5$ would in this way yield an ingot having composition tapering almost uniformly from the virtually pure compounds

at the extremities. This would not be true in the higher-segregating alloys; also it would be more difficult to initiate a liquid zone at the high-melting end in the other alloy systems.

Apparatus for Sequential Growth

As already described, the sequential growth technique required both step-freeze and zone growth facilities. The step-freeze furnaces were resistance-heated in both hot and cool zones, and when set for the growth of $\text{InAs}_x\text{Sb}_{1-x}$ the temperature profile in the transition region, (as measured with a thermocouple in the empty furnace) was practically linear with a gradient of $60^\circ\text{C}/\text{cm}$. A synchronous motor and gear train were used to move the quartz or alumina tube containing the ampoule. These furnaces were the ones used by Coderre (69C3) and others.

Two zone furnaces were built, the first being intended for $\text{InAs}_x\text{Sb}_{1-x}$; the second was an improved design, aimed at the $\text{GaAs}_x\text{Sb}_{1-x}$ system. The zone heaters were intended for sequential growth, and since this did not require reaching all liquidus temperatures, they were designed for maximum temperature gradient and a short overall length. The temperature gradient is as much limited by the cooling means as the heating means, therefore water-cooled jackets were positioned closely adjacent to each side of the zone heaters. The internal diameter of the cooling jackets involves a compromise; if too large, the temperature gradient is lower than it could be; if too small, the ingot and ampoule within the cooling jackets may be cooled below the level at which As or Te-dopant vapour might condense. The temperature profile as measured

in the empty furnace was found to be an unreliable guide, but some information on this point was obtained by fitting a thermocouple inside a graphite rod, to simulate an ingot. From data obtained in this way, and by comparing the observed zone length with the theoretical value predicted from the empty furnace profile, it is believed that the gradient in furnace no. 1 under operating conditions was only $110^{\circ}/\text{cm}$, and not $250^{\circ}/\text{cm}$ as measured in the empty furnace.

Furnace no. 2 was designed to improve the temperature gradient, and for this it was necessary to reduce the diameter of both the heater and the cooling jackets to the minimum. The zone heater was constructed by winding 1.8 mm diameter Kanthal wire on a 1/2-inch diameter rod, then bending the helix into a loop, and cutting the ends short. The helix was fitted into an alumina ring, and encapsulated with furnace cement, leaving a gap at the top so that the liquid region and both interfaces could be observed. This gap was covered with a quartz window. When assembled in the furnace, each wire end was clamped to one of the cooling jackets, between which the electrical supply of about 10 volts at 30 amperes was applied. In this way the contacts were kept cool, which is essential to long life of Kanthal wire. Fig. 2.1.1 shows a cross-sectional view of the heater and cooling jackets. It seemed impractical to attempt to control the liquid zone temperature, this being distinctly lower than the temperature within the heating element. Instead, the line power was supplied through a voltage-stabilizing transformer, then a variable-ratio transformer (Variac type), and finally through a step-down transformer to the heater ,

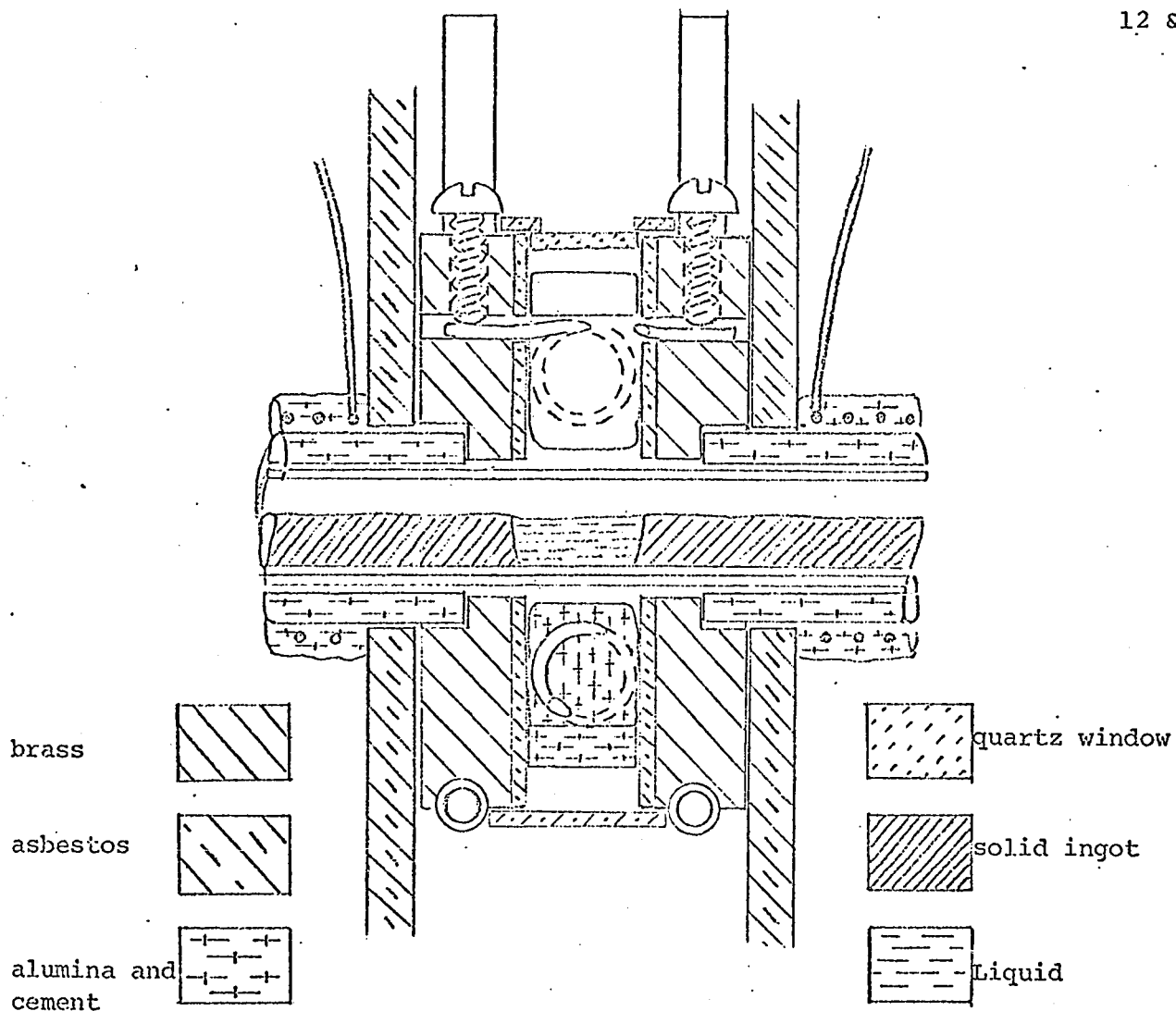


Figure 2.1.1. Cross-sectional view of zone heater, water-cooled jackets and heated "cool" zones.

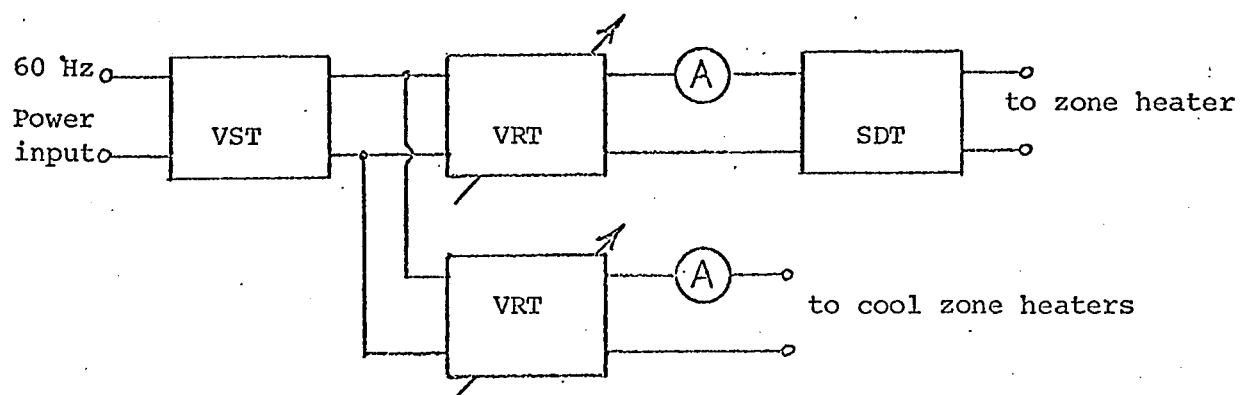


Figure 2.1.2 Schematic diagram of electrical power supplies for zone furnace.

as shown in Fig. 2.1.2. The cool zones were supplied with stabilized power by the same system, as shown. To minimize temperature fluctuations due to air currents, all heated regions were thoroughly insulated with asbestos cloth and the like. The cooling water pressure was stabilized, but its temperature was not, although this could have been easily done using a water reservoir as a heat exchanger.

Preparation of Ingots

Most ingots were prepared by direct synthesis from the elements: Ga, In, As, Sb, and Te dopant; such ingots had a clean appearance, and there were no signs of non-stoichiometric inclusions; these should not be expected, since the conditions for good alloy growth achieve this automatically. In principle the complete sequential process could be done using a single ampoule, and several ingots were grown in this way, but the following procedure avoids failures caused by the tendency of III-V compounds to stick to quartz on freezing.

Stoichiometric proportions of the elements were sealed into a quartz ampoule of 13 mm ID in the usual way, except that when As was present, the ampoule was made longer, with a dimple to confine the liquid to the usual length, as in Fig. 2.1.3(a). The extended portion of the ampoule was essential, to prevent explosion due to As vapour pressure. In all cases, the ampoule was evacuated and back-filled with argon to 1/3 atm. pressure before sealing. It was then driven mechanically at several cm/hr into the heated step-freeze furnace, with the extension portion entering last, until only the tip of the extension remained in the

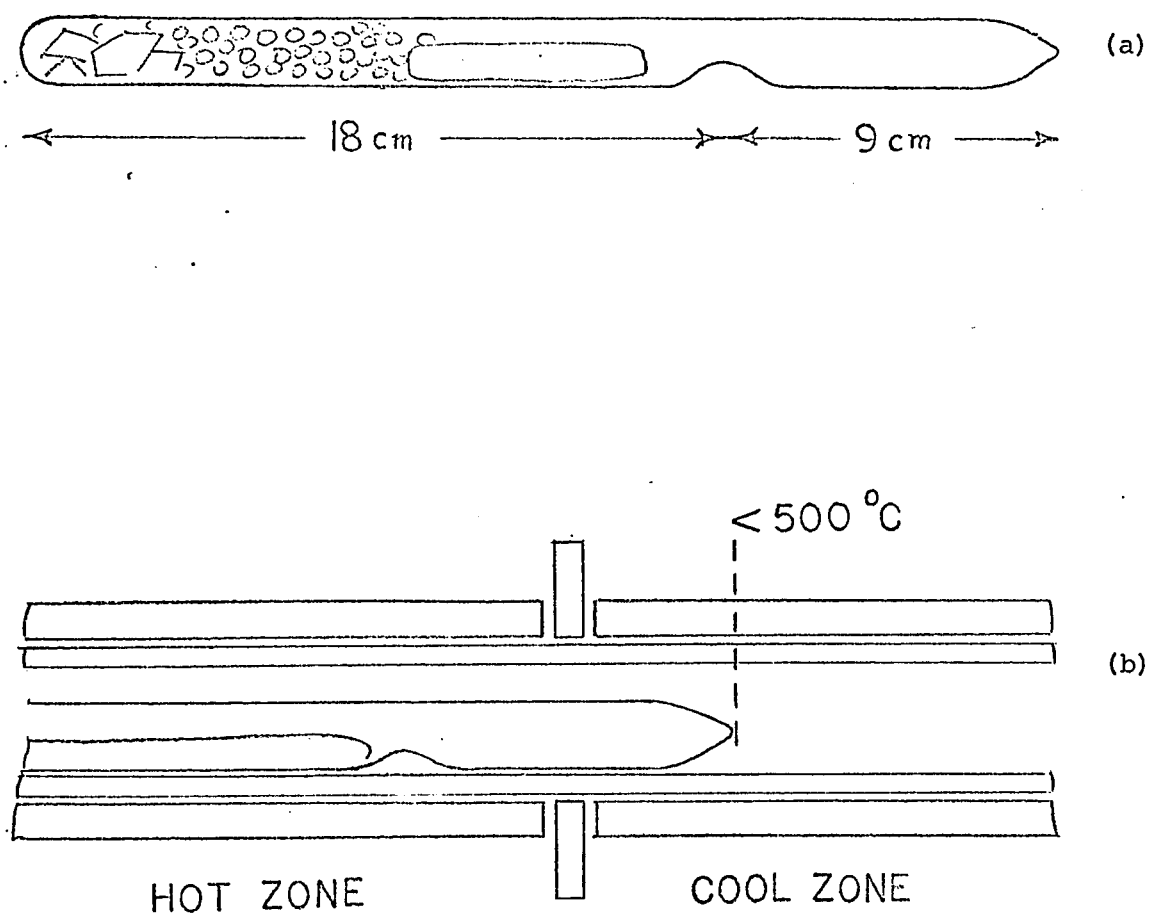


Figure 2.1.3 Synthesis of alloys from elements containing arsenic;

- (a) ampoule, including condensation region to prevent pressure build-up;
- (b) positioning of ampoule within furnace.

cool zone, as in Fig. 2.1.3(b). Unreacted As could thus condense in the tip, which was always below 500°C , and no explosions occurred.

The ampoule was left in the furnace overnight, then driven back into the cool zone at the same speed as before, and a current of nitrogen gas passed through the furnace from the cool end. The ampoule would usually crack slightly, but there was no problem with escaping As vapour, since the residual liquid was very depleted in arsenide by the time the crack occurred, and the nitrogen gas prevented oxidation. The ingot was transferred into a new ampoule containing a boat, which was made from 12 mm OD quartz tubing and flame-coated with vaporized quartz to prevent sticking. The ingot was driven again into the step-freeze furnace, and step-frozen at a rate chosen according to the desired taper in composition. The ingot was then given one or two zone passes within the same ampoule. There was little sign of condensation on the walls of the ampoule after the step-freeze process, but during the slow zone growth this was more noticeable, especially when Te was used. Ideally, the upper half of the water jackets should have been further away from the ampoule, since thermal conduction along the ingot and boat affects mainly the lower half of the ampoule.

2.2 THEORY RELATING TO GROWTH

Inhomogeneous growth

It is well known that inhomogeneous growth can occur in alloys under certain conditions. By inhomogeneities are meant semi-microscopic fluctuations in composition, and not the major variations along the length or breadth of ingots. In homogeneous alloys, the constituent species are randomly distributed among the available lattice sites, but long-range order is preserved, as proved by X-ray diffraction. In our ternary alloys, the random distribution is confined to one sublattice. Only on a submicroscopic scale, say in a $50 \text{ \AA}$ cube, are the random fluctuations significant.

In alloys which form solid solutions at all compositions the major (if not only) reason for inhomogeneous growth was explained by Rutter and Chalmers (53R1), a comprehensive account being given by Chalmers (64C1, chap. 5), as due to constitutional supercooling. This occurs when the growth rate exceeds a critical value which is characteristic of the particular alloy system and the temperature gradient at the growth interface, and is caused by excessive depletion of the higher-melting component from the liquid at the growth interface. Other possible causes of inhomogeneous growth are discussed at the end of this section.

The Variation of Composition along Ingots

Compared to the extensive literature on conditions affecting growth, references to the dissolution conditions are few. Partly this reflects the greater importance of growth conditions in determining the

properties of the final solid, but it should also be noted that the problem assumes practical importance only for those liquid/solid systems having widely separated liquidus and solidus curves on the phase diagram. Otherwise, it is sufficient for practical purposes to consider dissolution as simply "melting", thus ignoring the influence of the liquid composition on the dissolution process.

For study of the variation of composition along ingots the well-known rules relating growth to the system phase diagram were extended by formulating rules covering dissolution. Partly this was done by considering experimental conditions as reported in the literature on non-stoichiometric growth techniques such as the "travelling solution zone" method, and partly by requiring reciprocity between growth and dissolution processes at vanishingly-slow growth rates. There remained some doubt as to the validity of these rules until they were verified by observation, especially in the sequential growth of $\text{GaAs}_x\text{Sb}_{1-x}$, which provided a critical test since the furnace was designed to provide a short liquid zone of steep temperature gradient rather than high temperatures per se, and the liquidus temperatures could not be reached except at the extreme GaSb-rich end of the range.

The rules which were formulated in accordance with these ideas may be stated concisely as follows.

(1) The solid and liquid compositions and the temperature at the growth interface are mutually related by corresponding solidus and liquidus points on the phase diagram.

(2) The liquid composition at the dissolution interface (if any) is related to the interface temperature by a liquidus point on the phase diagram.

(3) No mixing occurs in the solid.

(4) Perfect mixing occurs in the liquid.

(5) No bulk liquid will form (in any reasonable time) until the liquidus temperature of the solid is reached.

Rule (1) implies that dissolution would occur at the growth interface during an upward fluctuation in temperature, and rule (2) implies that growth would occur at the dissolution interface during a downward fluctuation in temperature. However, unlike the freezing solid, the dissolving solid is not generally in equilibrium with the liquid adjacent to it; dissolution continues so long as the temperature at the interface exceeds the liquidus point of the adjacent liquid, regardless of the solid composition, except insofar as this influences the liquid composition. Inherent in these rules is the neglect of any chemical-kinetic rate limitations at the interfaces. Rule (3) should be satisfied in III-V alloys, considering the long annealing required for reaching equilibrium in powder mixtures, (62W1).

When rules (1), (2) and (4) apply, it follows that the growth and dissolution interfaces are at the same temperature; however, rule (4) fails more often than the others. Due to imperfect mixing, the liquid near the growth interface becomes depleted by segregation of the higher-melting component, with consequent fall in freezing point; near the dissolution interface the liquid composition inclines towards that of

the dissolving solid. In the steady state zone growth of a uniform ingot, both interfaces will therefore lag behind the symmetrical positions they would otherwise occupy, relative to the zone heater. For a high enough rate of travel of the zone heater, the efficiency of mixing deteriorates to the point that the liquid composition at the dissolution interface approximates to that of the solid. In that case, the dissolution interface will only continue to advance if the temperature imposed by the zone heater exceeds the liquidus temperature of the solid; otherwise it will lag behind until the growth interface catches up with it.

Rule (5) summarizes the difficulty already mentioned in Section 2.1, of initiating a liquid zone in a uniform starting ingot, which was solved by introducing the sequential process. The growth rate was chosen to be slow enough that the liquid zone could propagate through regions of higher-melting composition, carrying with it enough of the low-melting component to make this possible. This process is very similar to the one known as "travelling solution zone", which is normally associated with a metal-rich stoichiometric) liquid zone.

In order to study the variation of composition along ingots in a more quantitative way, rule (4) was replaced by a model which was adapted from the work of Burton et al (53B1), (see also Chalmers, 64C1) on impurity segregation in Ge during growth by the Czochralski method, in which liquid mixing is primarily due to mechanical rotation of the seed crystal. In resistance-heated horizontal growth, the liquid mixing is normally due only to convective stirring. According to the model, the

liquid is perfectly mixed everywhere except within thin stagnant layers at the growth and dissolution interfaces, caused by viscous drag. Burton et al offered a theoretical interpretation for the stagnant layer width δ in terms of the mechanical stirring parameters. In other references to stagnant layers, Wagner (54W1) has discussed convective mixing caused by the variation of density with composition in metal castings, and Abe (57A1) has discussed convective mixing in Sb-doped Ge, where the density variation was due to temperature gradients. Due to ignorance of the relevant variables in the present case, δ was regarded as an adjustable parameter, to be determined from experimental profiles. The mixing which occurs across each stagnant layer is the resultant of two opposing effects: the interdiffusion of components due to composition gradients within the layer, and the bulk flow due to movement of the stagnant layer with the advancing interface.

In order to avoid mathematical complications, the effect of the furnace heater was represented as a one-dimensional temperature profile, which is unaffected by the presence and movement of the ingot itself. The temperature profiles were usually found to be linear over the ranges of interest, but this is not essential to the analysis.

For a one-dimensional, steady state analysis we chose a coordinate u with origin at the growth interface, and moving with it, so that growth at rate R implies fluid flow at rate R into the stagnant layer towards the interface. Defining the higher-melting component as the solute, so that its concentration is x in our notation, the net

solute flow is the resultant of the diffusion flow and the bulk flow. This must be uniform through the layer, and equal to the rate of solute incorporation into the solid, i.e.

$$D \frac{dx}{du} + Rx(u) = R x_s \quad 2.2.1$$

where D is the diffusivity and x_s is the composition freezing out.

At $u = \delta$ the composition is that of the bulk liquid, i.e.

$$x(\delta) = x_L \quad 2.2.2$$

Assuming that D is uniform through the layer, the solution of eq. (1) is

$$x(u) = (x_L - x_s) e^{\Delta(1 - \frac{u}{\delta})} + x_s \quad 2.2.3$$

where Δ is a normalized growth rate:

$$\Delta = \frac{R\delta}{D} \quad 2.2.4$$

At the interface, let $x = x_F$, then eq. 2.2.3 yields the relation of Burton et al:

$$\frac{x_s - x_F}{x_s - x_L} = e^{\Delta} \quad 2.2.5$$

The phase diagram defines a second relation between x_s and x_F :

$$x_s - x_F = \alpha_F \quad 2.2.6$$

where α_F is the length of the tie line relating x_S and x_F .

At the dissolution interface the expression corresponding to eq. 2.2.5 is

$$\frac{x_O - x_M}{x_O - x_L} = e^{-\Delta_M} \quad 2.2.7$$

The exponent has an explicit minus sign so that Δ_M the normalized dissolution rate is positive. As previously made clear, there is no relation corresponding to eq. 2.2.6 at the dissolution interface; on the other hand, (as if to compensate) the solid composition x_O is known.

The liquid composition x_M at the dissolution interface, and the compositions x_O , x_L , x_F and x_S are further related by solute conservation. Thus, in a small movement δa of the heater, the change in x_L is

$$\delta x_L = \frac{\{x_O(b) - x_L\} \delta b - \{x_S(c) - x_L\} \delta c}{l + \delta b - \delta c} \quad 2.2.8$$

where δb and δc are the movements of the dissolution and freezing interfaces at b and c respectively, and l is the liquid zone length, assumed to be much greater than δ . δb and δc are given by

$$\delta b = \delta a - \Theta_M \delta x_M / G \quad 2.2.9$$

$$\delta c = \delta a + \Theta_F \delta x_F / G \quad 2.2.10$$

where Θ_M and Θ_F are slopes of the liquidus curves at x_M and x_F on the phase diagram, and where G is the temperature gradient imposed by the heater.

Eqs. 2.2.4 to 2.2.10 may be solved numerically for successive positions of the heater, and the complete process traced out from initial melting to final freezing. In other types of growth the dissolution and freezing processes may not occur simultaneously, but the procedure is general. In the numerical work, for each increment δa the following sequence of equations was evaluated iteratively until a stable value of x_S was attained. (As described below, two modifications were made to ensure convergence.)

$$\Delta_M = \Delta_1 r_M \quad 2.2.11$$

$$x_M = (x_L - x_O) \exp(-\Delta_M) + x_O \quad 2.2.12$$

$$k_O = 1 + \alpha_F/x_F \quad 2.2.13$$

$$\Delta = \Delta_1 r \quad 2.2.14$$

$$x_S = x_L k_O / \{k_O - (k_O - 1) \exp(-\Delta)\} \quad 2.2.15$$

$$x_F = x_S/k_O \quad 2.2.16$$

δb , δc and δx_L were obtained from eqs. 2.2.9, 2.2.10 and 2.2.8, then

$$r_M = \delta b/\delta a \quad 2.2.17$$

$$r = \delta c/\delta a \quad 2.2.18$$

In these expressions, Δ_1 is the value of Δ_M and Δ corresponding to dissolution and growth at the nominal rate, so that $\delta b = \delta c = \delta a$. r_M and r are dissolution and growth rates respectively, relative to the nominal rate R . The segregation coefficient k_0 as defined by eq. 2.2.15 varies in InAsSb_{1-x} from 47, when x is very small, down to unity as x approaches unity. α_F , θ_M and θ_F were obtained from data representing the phase diagram, and x_0 values were obtained from the composition profile initially existing in the ingot, e.g. chill-cast, step-freeze, zone grown, etc. The iteration was often found to be divergent, due to the sensitivity of δc to errors caused by rapid changes in x_0 or in x_s . This difficulty was overcome by artificially damping all changes in x_M and r ; specifically: about 10% of the values defined by eqs. 2.2.12 and 2.2.18 were added to complementary portions of the previous values. A simplified flow diagram for the complete calculation is shown in Fig. 2.2.1. Detailed numerical work of this type may be avoided in many cases; for example, the relative growth rate can be obtained from eqs. 2.2.10 and 2.2.26 in the form

$$r = \frac{dc}{da} = 1 / \left(1 - \frac{\phi_s}{G} \frac{dx_s}{dc} \right) \quad 2.2.27$$

where ϕ_s is the slope on the phase diagram of the solidus curve at x_s . The profile slope dx_s/dc may be measured experimentally, or obtained from the relation

$$\frac{dx_s}{dc} = \frac{dx_F}{dc} \frac{\theta_F}{\phi_s} \quad 2.2.28$$

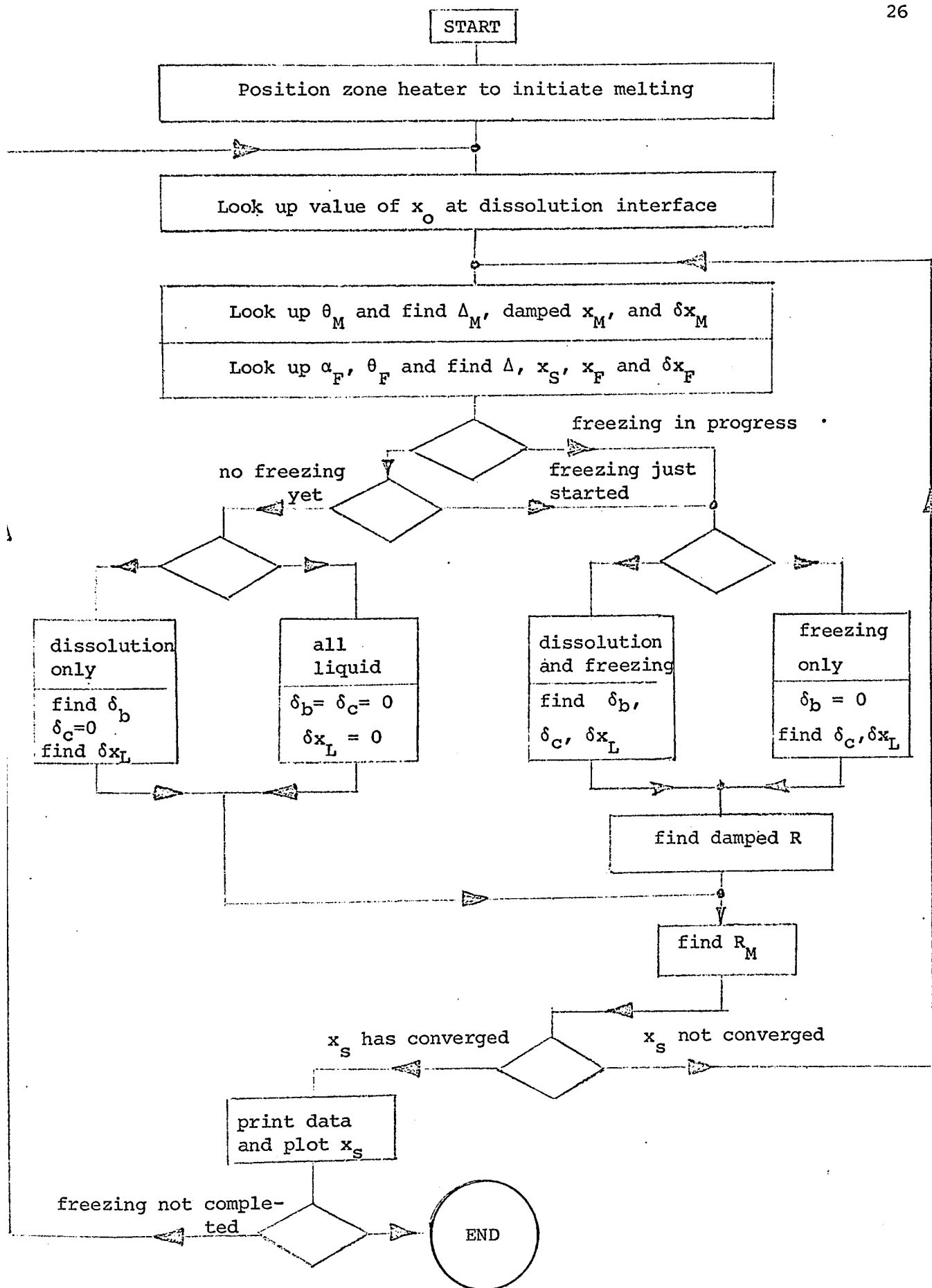


Figure 2.2.1 Flow diagram for calculation of ingot composition profiles, using stagnant-layer model.

in cases where this can be evaluated. For example, if there is no dissolution and perfect mixing, it becomes, using eq. 2.2.8,

$$\frac{dx_s}{dc} = \frac{x_s}{\ell} \cdot \frac{(1-k_o)}{k_o} \cdot \frac{\theta_L}{\phi_s} \quad 2.2.29$$

For this simple case, the relative growth rate becomes

$$r = 1/\{1 + \frac{x_s}{G\ell} \cdot \frac{(1-k_o)}{k_o} \cdot \theta_L\} \quad 2.2.30$$

Another useful expression, due to Chalmers (64C1), (53R1) may be obtained from eqs. 2.2.3 and 2.2.5, giving the gradient of liquidus temperature $\Psi(u)$ through the stagnant layer:

$$\Psi(u) = \frac{\partial T_L}{\partial u} = \frac{\partial T_L}{\partial x} \frac{\partial x}{\partial u} = \theta(x) (x_s - x_F) e^{-Ru/D} \quad 2.2.31$$

(Note that Ψ is a gradient in real space, while θ and ϕ are slopes on the phase diagram.) For a given furnace gradient and given alloy system, the value of $\Psi(o)$ obtained from eq. 2.2.31 sets an upper limit on the stable growth rate. Since eq. 2.2.31 does not contain δ it appears that the maximum stable growth rate of a given composition x_s is independent of the rate of stirring. Practical workers have stated the opposite; they could be correct if δ were made so small that any inhomogeneities were small enough in size to disappear by interdiffusion in the solid.

Application to Prior Work

If perfect mixing is assumed, so that $x_M = x_L = x_F$, the numerical method can be reduced to a non-iterative procedure, by eliminating

δb and δc from eq. 2.2.8. Fig. 2.2.2 illustrates profiles computed in this way, due to step-freezing various starting compositions of $\text{InAs}_x\text{Sb}_{1-x}$.

As a test for the stagnant layer theory, an experimental step-freeze profile for $\text{InAs}_x\text{Sb}_{1-x}$ (69C3) was chosen, and the starting composition was estimated as 0.175 from the area under the profile, allowing for the known total length of the ingot. A theoretical step-freeze profile was fitted to it, by choosing $\Delta_1 = 0.07 \pm .005$, as shown in Fig. 2.2.3. On the other hand, the theoretical profile for perfect mixing does not fit at all. It is of interest to ask what value of δ is implied by the value $\Delta_1 = 0.07$. Now the nominal growth rate was 0.5 cm/day, and the actual growth rate was initially very close to this. Unfortunately D is not known, but if we use the value $0.5 \times 10^{-4} \text{ cm}^2/\text{sec}$ assumed by Burton et al (53B1) for molten Ge we obtain $\delta = 0.6 \text{ cm}$. We might expect D to be somewhat less in the present case, where As-rich molecular groupings diffuse in a medium containing heavier atoms than Ge. This would reduce the value of δ .

It is also of interest to ask if constitutional supercooling existed at any time during growth. In terms of the assumed value of D , this may be answered by using eq. 2.2.3, from which we find that the maximum value of $\Psi(o)$ occurred in the range $0.6 \leq x_s \leq 0.8$, where R had fallen to about half the nominal rate, and we obtain $\Psi(o) \approx 66^\circ\text{C}/\text{cm}$, compared to the measured temperature gradient of $60^\circ\text{C}/\text{cm}$ in the empty furnace. This indicates some supercooling, but to be more precise we would need to know D and G more accurately.

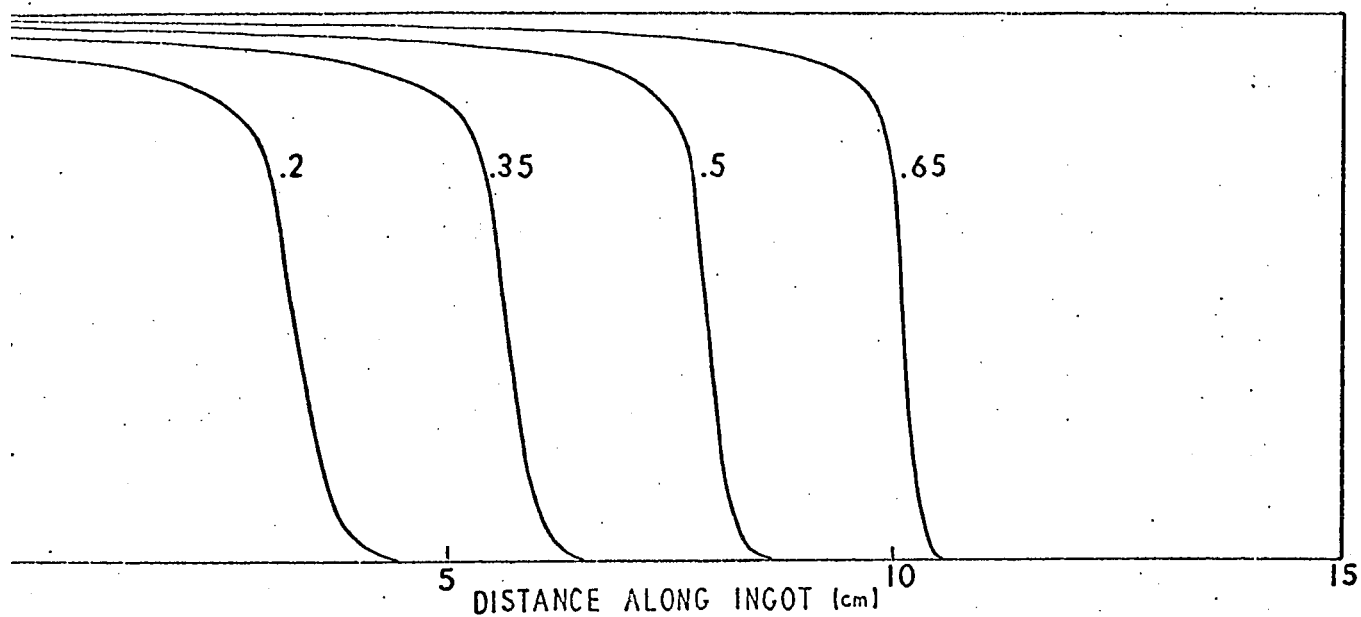


Figure 2.2.2. $\text{InAs}_x\text{Sb}_{1-x}$ theoretical step-freeze profiles for average compositions as labelled, assuming perfect mixing.

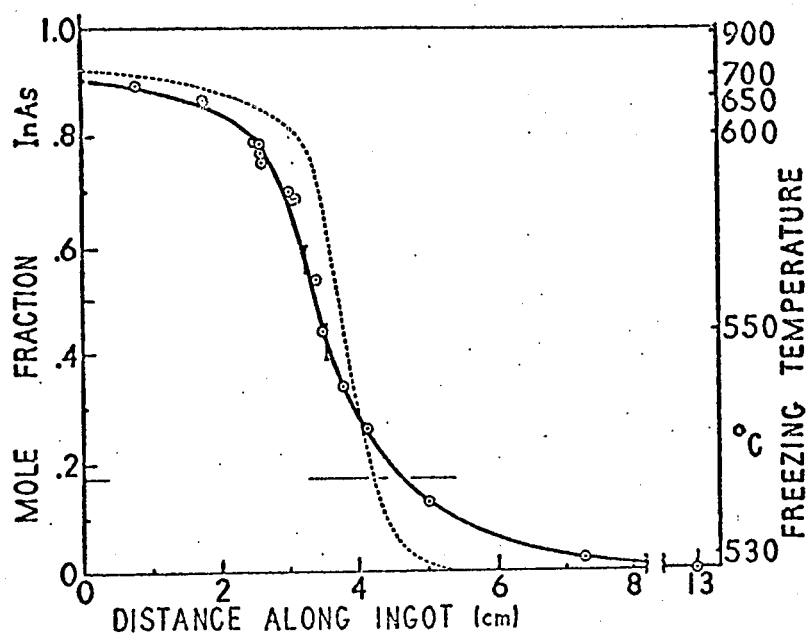


Figure 2.2.3. $\text{InAs}_x\text{Sb}_{1-x}$ theoretical step-freeze profile for average composition 0.175, fitted to experimental points of Coderre (69C3). Theoretical curve for perfect mixing (dotted) does not fit data.

Since the experimental profile does indicate some composition inhomogeneity in this range, it is of interest to look at a case of definite failure to obtain homogeneity, as reported by Woolley and Warner (64W1) for the same alloy, using the gradient freeze technique. Their gradient was $7^{\circ}\text{C}/\text{cm}$ and the nominal growth rate was $4/7 \text{ cm/day}$, obtained by programming the temperature downward at $4^{\circ}\text{C}/\text{day}$, but the estimated actual rate fell to a minimum of only $.02 \text{ cm/day}$, due to the shallow gradient. The observed inhomogeneities, which were severe throughout the range $0.2 \leq x_s \leq 0.8$, were attributed to constitutional supercooling. However, their experimental profile was more abrupt than our previous example, indicating very efficient mixing. If we assume that the mixing was perfect; the slope of the most abrupt region is given by eq. 2.2.29 as -1.7cm^{-1} , in agreement with the experimental profile. This is not surprising, for at such slow growth rates diffusion alone would account for quite efficient mixing, as is easily verified by setting δ equal to the remaining liquid length, which was about 7 cm during growth in the abrupt region. With good mixing, we might expect the liquidus gradient at the interface to be very small. Table 2.2.A shows the gradients given by eq. 2.2.31, the growth rates being obtained from eq. 2.2.30; from this it appears that $\Psi(0)$ remained almost constant and slightly less than the furnace gradient. A smaller value of D would reduce $\Psi(0)$, so it is questionable if the observed inhomogeneity was caused by supercooling.

Table 2.2.A

Theoretical liquidus gradients $\Psi(0)$ for a gradient-freeze ingot.

x_s	.1	.2	.4	.6	.8	.9	.95	.975
R cm/day	.11	.062	.038	.025	.023	.046	.12	.25
$\Psi(0)^{\circ}\text{C/cm}$	5.3	5.7	6.7	6.2	6.1	6.9	8.2	7.8

The short-term temperature stability was stated to be $\pm 0.2^{\circ}\text{C}$, and the question arises, whether temperature fluctuations could account for the observed inhomogeneities. Suppose that an abrupt change in external conditions caused an internal change of -0.2°C during a period (determined by thermal inertia) of 10 seconds. During this interval the steady growth increment (apart from fluctuations) would be $2.7 \times 10^{-6}\text{cm}$, and the interface temperature would drop by very nearly the programmed drop, namely $3 \times 10^{-4}^{\circ}\text{C}$, (because the steady growth increment is only 1/25 of the nominal value). If liquid mixing remained nearly perfect during the fluctuation, the interface would advance $1.3 \times 10^{-3}\text{cm}$, and drop nearly 0.2°C in temperature. However, during the 10-second transient period, liquid mixing would be restricted to a distance of about one "diffusion length", i.e. $\sqrt{10D} \approx 0.02\text{cm}$. Since this is only a fraction 0.003 of the total liquid region, the relative growth rate given by eq. 2.2.30 would be reduced to only 0.003 times the already small value, so the actual advance due to the fluctuation would be only $3.9 \times 10^{-6}\text{cm}$, which is little more than that due to steady growth. It seems probable that inhomogeneities of these small dimensions would be smoothed out by interdiffusion in the

solid, during the many days spent just below the solidus temperature. The conclusion is that the system possesses a "diffusion inertia" against rapid fluctuations. Long term fluctuations would have even less effect, and allowance for latent heat of freezing would increase the inertia effect slightly. Thus, neither constitutional supercooling nor external disturbances seem able to account for the observed inhomogeneities completely.

Possibility of Spontaneous Inhomogeneities

The question arises whether alloy growth is necessarily homogeneous if there is no constitutional supercooling. Suppose the growth interface already has inhomogeneous composition, the problem is to explain how this might be self-perpetuating. It was noticed by Antypas and James (70A1) that when $\text{GaAs}_x\text{Sb}_{1-x}$ is deposited epitaxially from Ga-solution onto GaAs substrates, the initial deposit is almost pure GaAs, changing exponentially within the first 4 microns, then only slowly due to depletion of As from the liquid. (This copying effect is to be expected, since deposition occurs at a composition which minimises the free energy of the system, including the energy of the dislocations due to mismatch. Only in steady state growth are the solid and liquid compositions represented by the phase diagram.)

To apply this principle to our supposed inhomogeneities in growth of a mixed As, Sb system, denote regions of above average As composition as A cells, and the rest as B cells. Due to the copying effect, growth will occur in a manner which reproduces the cellular

structure, but with composition evolving towards the average within a distance of several microns. However, A cells will grow ahead of B cells because their freezing point is higher than the actual temperature. The advance would be limited by the temperature gradient if this were sufficiently great, but this is unlikely, since the temperature increase within 4 microns is only 0.2°C if the gradient is $500^{\circ}\text{C}/\text{cm}$. By contrast, if the smallest significant deviation in composition is taken as 0.01, the decrease in freezing point due to evolution would be at least 1°C in $\text{InAs}_x\text{Sb}_{1-x}$, so that evolution should limit the advance of A cells in practical cases. In $\text{GaAs}_x\text{Sb}_{1-x}$ the solidus slope appears to be very small for $x < 0.4$, so practical furnace gradients might be effective in limiting the advance of A cells in that case.

Due to the copying effect and to the enhanced growth of A cells, very small inhomogeneities due to various fluctuations would be magnified. Whether such a magnification effect would apply to the spontaneous fluctuations, imposed by the laws of probability on the microscopic composition, remains uncertain; this would appear to need a more quantitative discussion than the above.

Application To Zone and Sequential Growth

To illustrate the application of the forgoing numerical method to the prediction of zone growth profiles in $\text{InAs}_x\text{Sb}_{1-x}$ Fig. 2.2.4 illustrates the results to be expected from using a relatively long liquid zone, for various uniform initial compositions, and assuming a reasonable mixing parameter: $\Delta_1 = 0.07$. Woolley and Warner (64W1)

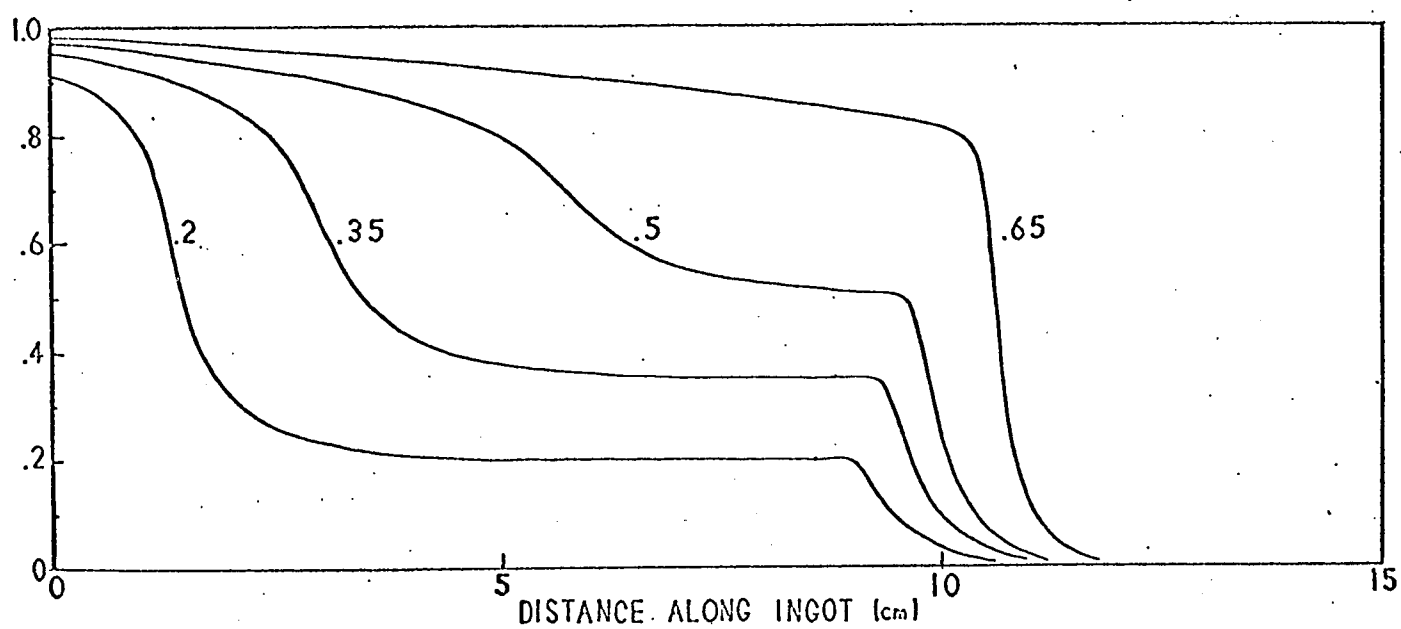


Figure 2.2.4. $\text{InAs}_x\text{Sb}_{1-x}$ theoretical zone growth profiles for various average compositions as labelled, assuming same mixing parameter as in Figure 2.2.3.

anticipated that a longer zone might provide a smoothly-tapered profile, but this is not supported by Fig. 2.2.4. Before experimenting with sequential growth in $\text{InAs}_x\text{Sb}_{1-x}$ it was of interest to estimate what growth rate should be used in step-freezing the starting ingot, to yield a desirable taper in the final composition. Obviously, the growth rate should be many times the "normal" rate of 0.5 cm/day which yielded $\Delta_1 = 0.07$ experimentally. Fig. 2.2.5 shows the theoretical profiles for an equimolar starting composition ($x = 0.5$) for $\Delta_1 = 0.35, 0.69, 1.05$ and 1.40 , corresponding to growth at 5, 10, 15 and 20 times this rate. (As made clear in the theoretical discussion, these are nominal rates set by the drive mechanism, the actual rates being lower and varying.) Fig. 2.2.6 shows the profiles to be expected after one zone pass over these step-freeze profiles. Fig. 2.2.7 shows the predicted profiles for a starting composition $x = 0.4$, for a step-freeze at 10 times the normal rate, followed by two zone passes. For all the zone passes, it was arbitrary assumed that $\Delta_1 = 0.07$, but the exact choice makes little difference to the profiles.

Similar profiles were computed for $\text{GaAs}_x\text{Sb}_{1-x}$, using an estimated liquidus curve; (the phase diagram computed by Antypas and James (70A1) was not then available.) The results indicated that higher step-freeze growth rates would be needed for this system.

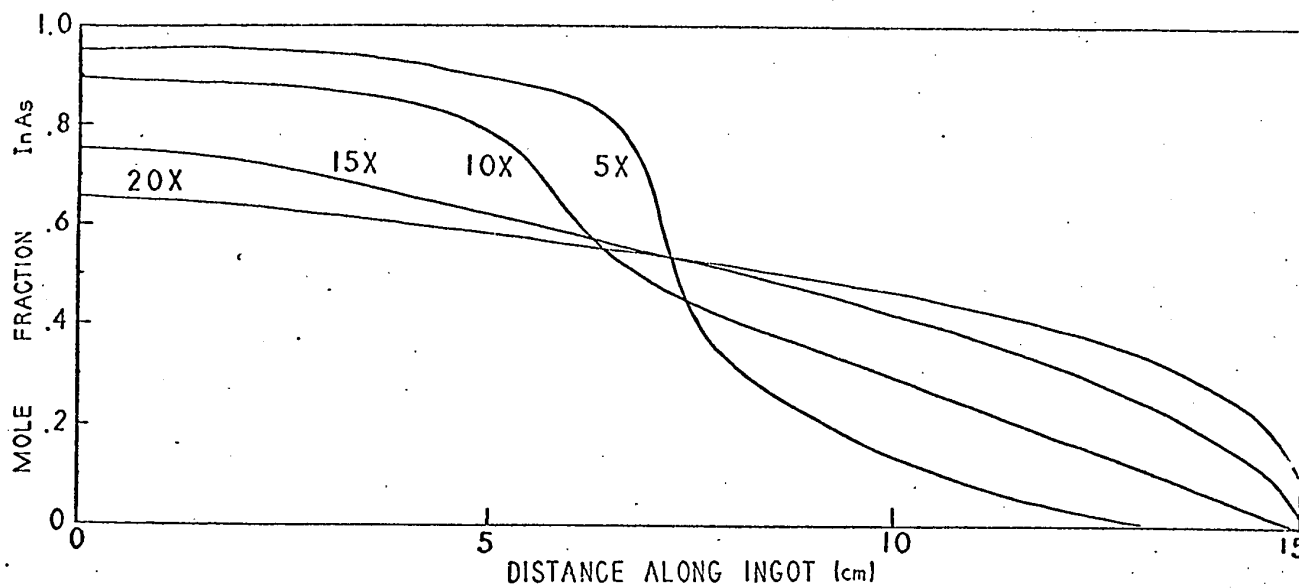


Figure 2.2.5. Theoretical profiles for $\text{InAs}_{0.5}\text{Sb}_{0.5}$ after rapid step-freezing at 5, 10, 15 and 20 times the usual speed of 0.5cm/day.

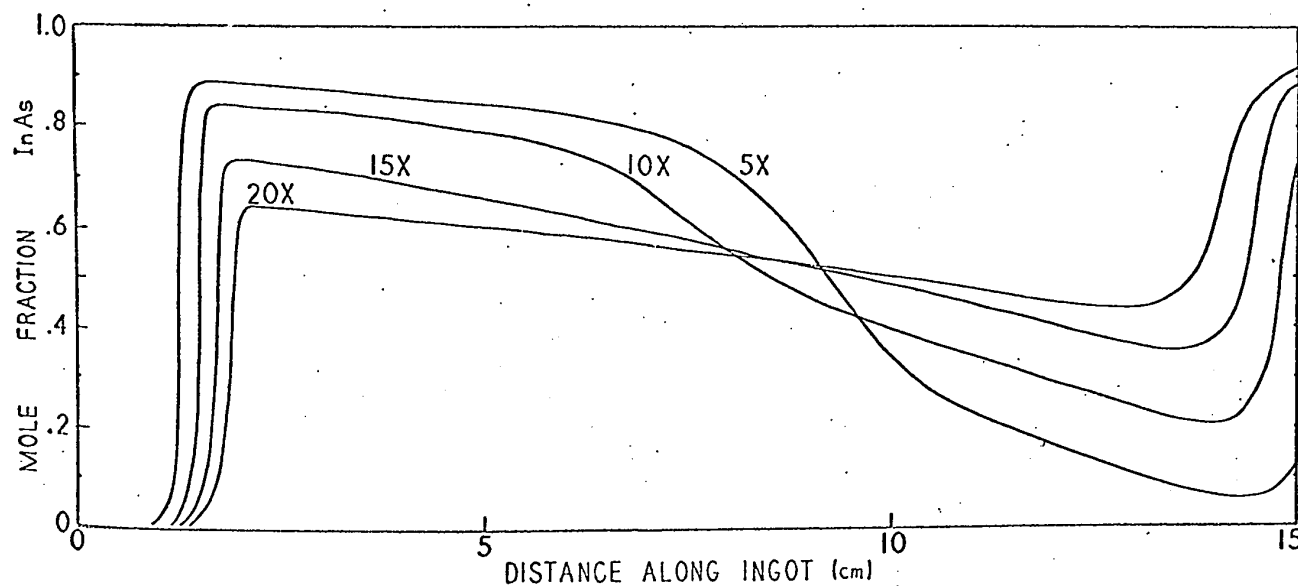


Figure 2.2.6 Theoretical profiles for sequential growth, after one zone pass from right to left over the step-freeze profiles of Fig. 2.2.5.

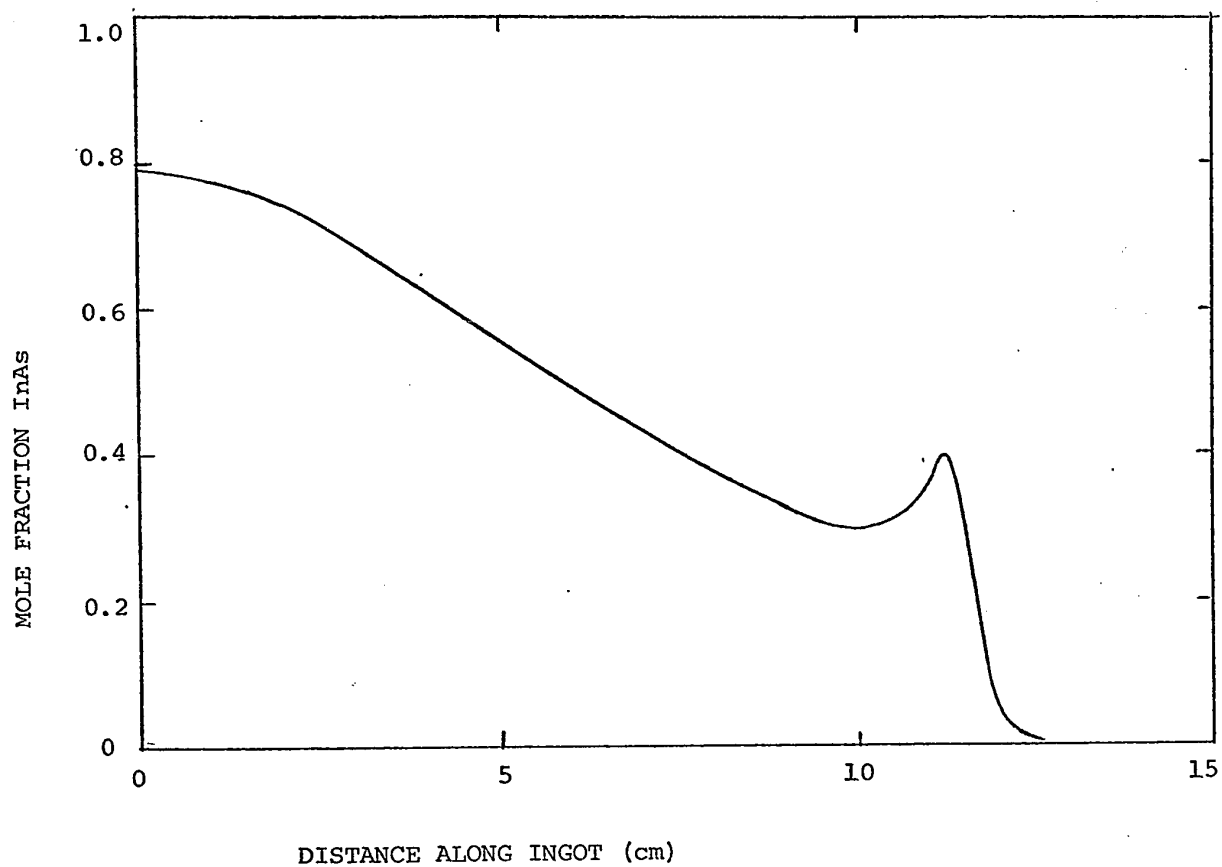


Figure 2.2.7. Theoretical profile for sequential growth of $\text{InAs}_{0.4}\text{Sb}_{0.6}$, with step-freeze at 10 times the "usual" rate, followed by both forward and reverse zone passes at low speed.

2.3 RESULTS

Practical Summary

Composition profiles and other relevant data on most of the ingots are detailed in this section. These results clearly demonstrate the value of sequential growth for the preparation of highly-segregating alloys, and although complete agreement was not found with the predictions of the computer simulations, the observed discrepancies were not such as to invalidate the general reasoning of Section 2.2.

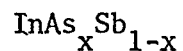
In all, thirteen ingots were completed, eleven of these by sequential growth techniques, and one each by standard step-freeze and by zone levelling respectively. The work was greatly hindered by the sticking of arsenides to quartz, which caused a total of eight failures due to cracked ampoules during rapid step-freezing. Failures were equally prevalent whether the ingots were prepared from mixtures of the compounds or by direct synthesis from the elements, and appeared to be the most likely when the ingredients were clean-looking and free from small fragments. (There is evidence that sticking could be avoided by tolerating somewhat oxidized ingots.) The failures occurred while a succession of measures aimed at preventing sticking were being tried, including internal grit-blasting of the quartz using an S.S. White Airbrasive machine¹, and the deposition of Al_2O_3 by the thermal oxidation of aluminum pyroxide. The preferred technique was described in Section 2.1.

Homogeneity and Composition

Cross-sections of about 0.06 cm thickness were taken at intervals along each ingot, and examined visually for grain size and for possible voids, and by conventional X-ray powder photography for information on homogeneity and lattice parameter. Since the pressure measurements are very sensitive to the composition in GaSb-rich materials, samples of these were powdered together with unalloyed GaSb of about the same Te-concentration, to provide calibration lines on the X-ray photographs. Compositions were determined from the lattice parameters, using the data of Woolley and Warner (64W1) for $\text{InAs}_x\text{Sb}_{1-x}$, and a Vegard line for $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ since this has been shown to be valid (62W1). A Vegard line was also assumed for $\text{GaAs}_x\text{Sb}_{1-x}$ (see Sections 6, 7).

Zone-growth $\text{Ga}_x\text{In}_{1-x}\text{Sb}$, and GaSb-rich or InSb-rich materials in the other systems, had large grain size of about 0.4 cm, except that the crystallites were subdivided by numerous twin boundaries. In $\text{InAs}_x\text{Sb}_{1-x}$ and $\text{GaAs}_x\text{Sb}_{1-x}$ the grain size decreased to about 0.1 cm at central compositions. Some $\text{InAs}_x\text{Sb}_{1-x}$ material contained hairline voids about .005 cm long, but only a few microns in width; they were very curved, therefore if they were caused by cracking, this must have occurred at high temperatures. Square specimens for electrical measurements were cut so as to eliminate voids; however these had little apparent influence on the mobilities as measured on complete cross-sections. Indeed, material containing voids showed identical mobilities to material having the same composition, ($x = 0.75$) from a different ingot, these mobilities exceeding those previously reported for the same composition, (68K2), (68C1). Voids were rare in alloys rich

in GaSb or GaAs, and did not correlate with the "resistance barriers" described in Section 3.2.



Preliminary experiments with growth rates and furnace power settings indicated that a speed of less than 0.5 cm/day would be needed for homogeneous growth. In this respect it should be noted that the actual rate of steady-state zone levelling equals the nominal rate regardless of the temperature gradient, rather than lagging behind as it does during growth of the steeply-graded part in a step-freeze ingot. During sequential growth, the actual rate leads the nominal rate during the first zone pass, and lags on the return pass if one is given, but these are small effects when the profile is smoothly tapered as it should be. Such effects, and similar ones at the dissolution interface, were followed by observation through the viewing windows, and provided information about the temperature gradient. In one test, the cooling water flow rate was reduced, and the liquid-solid interface shifted almost 0.1 cm to a new equilibrium position. This correlated with a rise in water temperature of 23°C at the outflow, from which the gradient was estimated as $(100 \pm 25)^\circ\text{C}/\text{cm}$, in agreement with the estimate of 110°C/cm mentioned in Section 2.1.

Following the preliminary investigations, three ingots were prepared by the sequential technique, using various growth rates as

listed in Table 2.3.A. These ingots were not doped.

TABLE 2.3.A

$\text{InAs}_x\text{Sb}_{1-x}$ ingots

(Numbers in parentheses give distance along ingot at which the growth rate was changed.)

#	initial x	mass (g)	length (cm)	Nominal growth rates, (cm/day)		
				step-freeze	1st zone	2nd zone
TZC 10	0.4	43	18	11	1.9	0.27(10)1.9
TZC 11	0.4	37	17	32	0.38(3)0.27	-
TZC 12	0.4	43	13	79	0.38	-

The composition profiles of these ingots are shown in Figs. 2.3.1 to 2.3.3., where the apparent electron concentrations and mobilities (Section 3.1) are also given. In ingot TZC10 the step-freeze growth rate was too slow; this was clear from visual inspection of the ingot at that stage, since InAs-rich material has a blue colour; consequently to save time only part of the final zone pass was done at low speed. In error, the speed was increased too early, and the central composition range was not homogeneous. The range $0.76 \leq x \leq 0.84$ was very homogeneous with high mobility, but showed the hairline voids discussed earlier. Ingot TZC11 gave a better profile, although a more gradual tapering would be preferred.

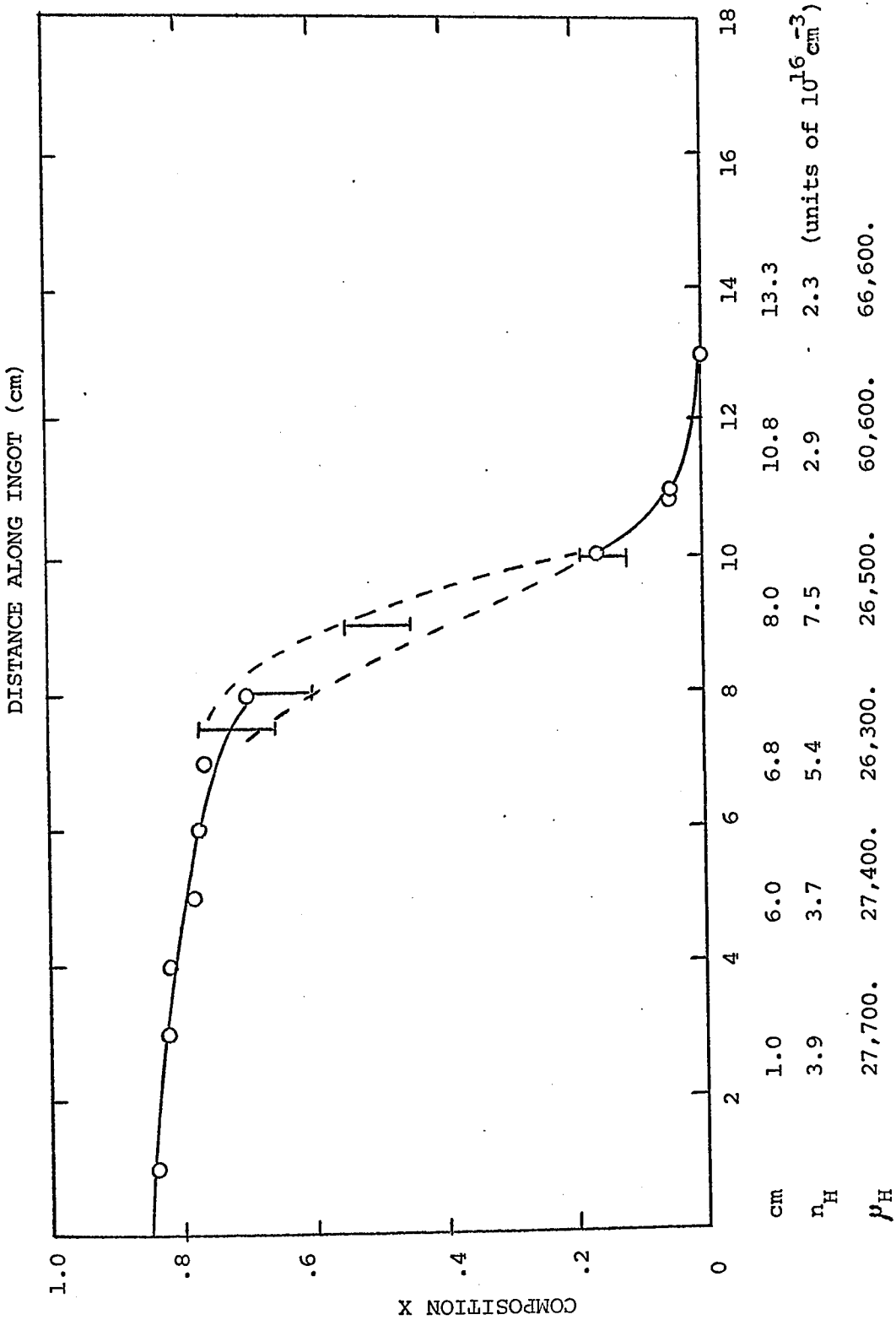


Figure 2.3.1. Experimental sequential growth profile for $\text{InAs}_{0.4}\text{Sb}_{0.6}$ (ingot TZClO).

The Table shows apparent electron density and mobility at various positions.

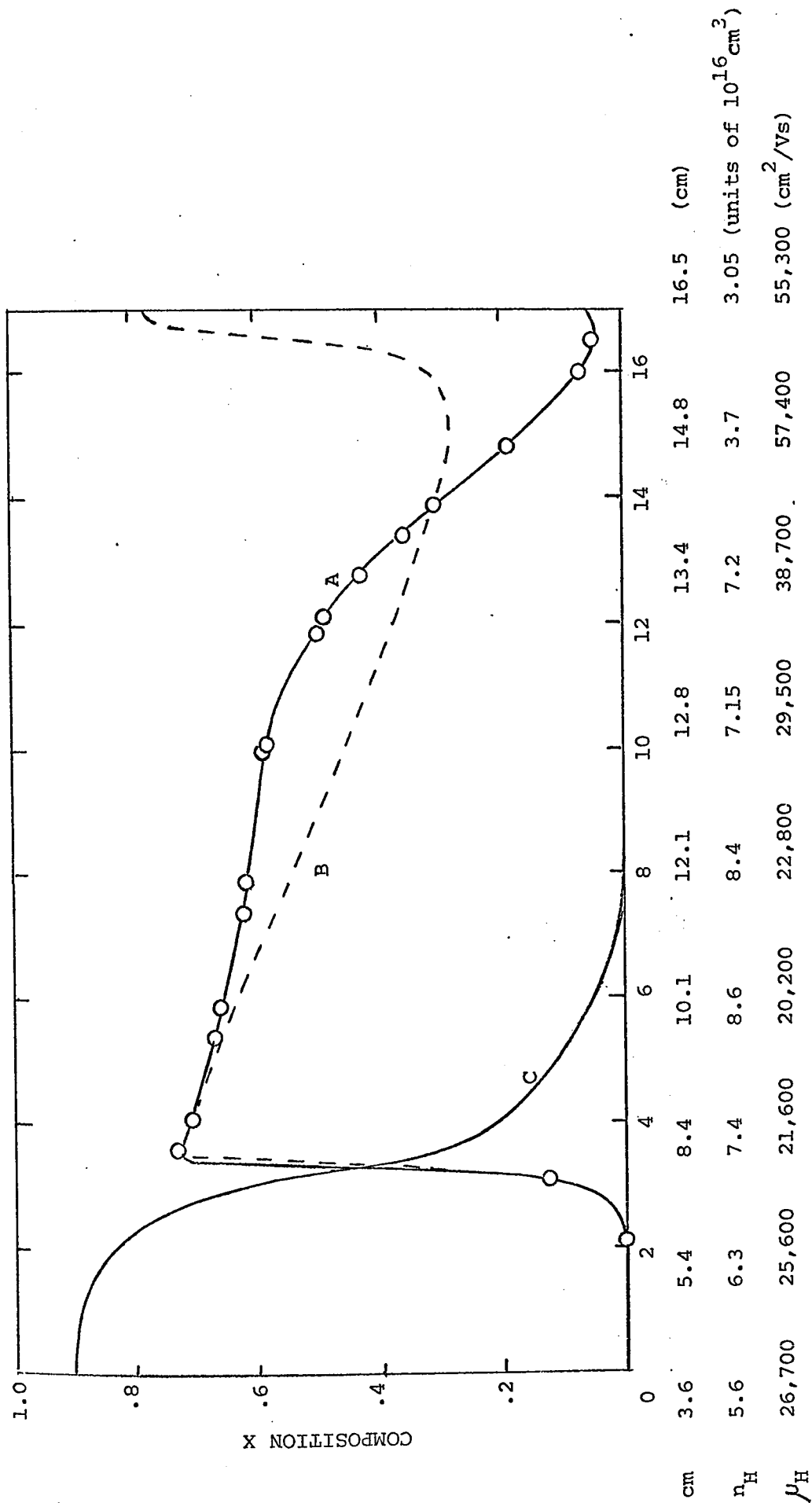


Figure 2.3.2 Experimental sequential growth profile (A) for InAsSb_{1-x} (ingot TZCl1), compared to theoretical curve (B), and to experimental step-freeze profile (C) taken from Fig. 2.2.3. The table shows apparent electron density and mobility at various positions.

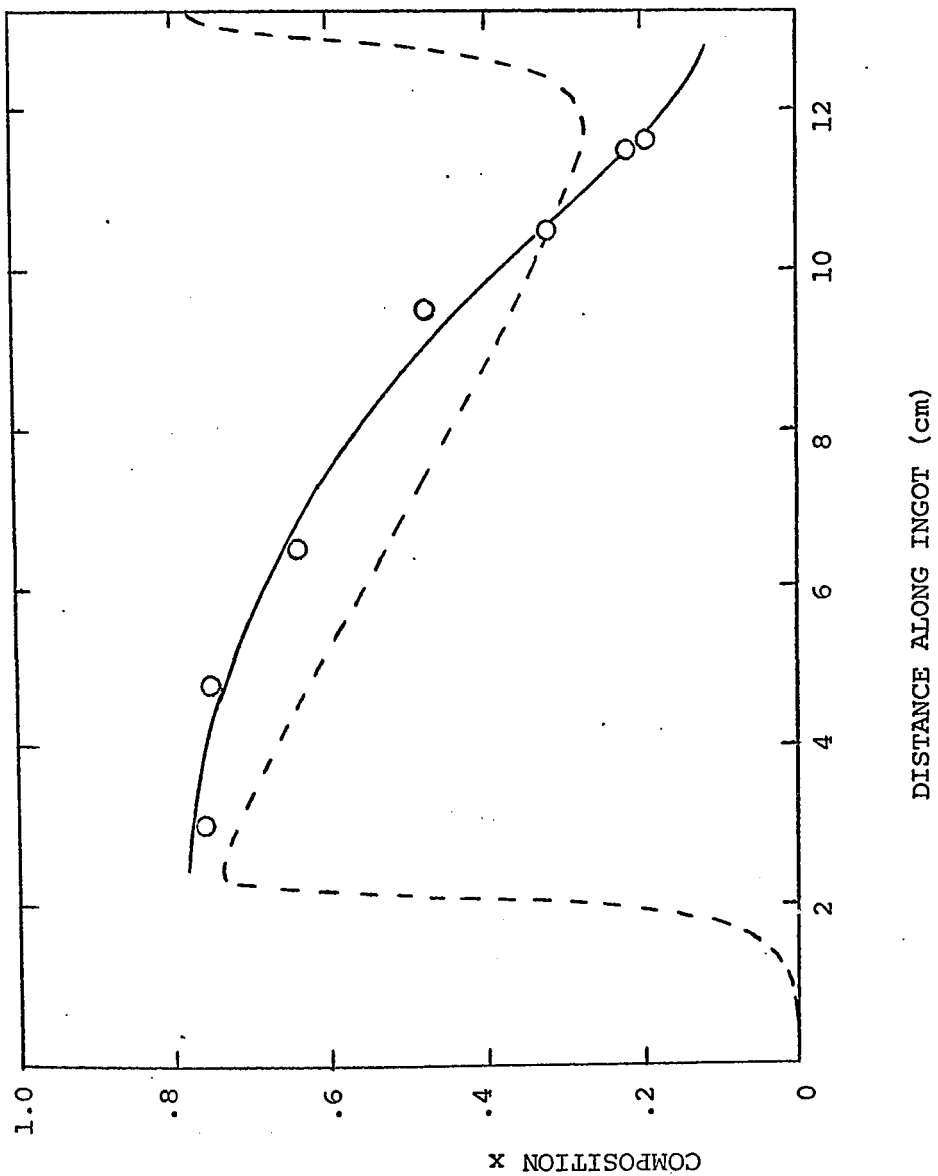


Figure 2.3.3. Experimental sequential growth profile for $\text{InAs}_{0.4}\text{Sb}_{0.6}$ (ingot TZCl2); The closest theoretical result is shown in the dotted curve.

Also shown in Fig. 2.3.2 are the step-freeze profile obtained by Coderre and discussed in Section 2.2, and a theoretical profile computed for sequential growth, with the step-freeze at a nominal growth rate of 10 cm/day. Better agreement could be found in the central region by taking a nominal rate of about half this, but this would increase the predicted initial transient, which was not observed at all. It should also be noted that the nominal growth rate used experimentally was 32 cm/day. The discrepancy between predicted and experimental growth rates to obtain a smooth taper is probably due to increased stirring at higher growth rates. This should have been expected, since the increased segregation must increase the density gradient, and hence the amount of convective stirring, which at low growth rates would be due to thermal gradient only. This may also explain the change of slope in the profile of ingot TZC11, since the stirring due to segregation would be very intense initially.

Ingot TZC12 indicates a near-ideal tapering of composition, but was not very homogeneous; this profile would have been a good starting point for a reverse zone pass, which was not given since the main object was to ascertain the degree of tapering. As before, there was no sign of the initial transient peak which the theoretical curve predicts. Fig. 2.3.4 shows the mobilities measured on various compositions at room temperature and pressure, in good agreement with those reported by Coderre and Woolley (68C1), but not with Kudman and Ekstrom, (68K2). The average composition in ingot TZC11 (defined by the area under the profile) measures 0.395, compared to the starting composition of 0.4;

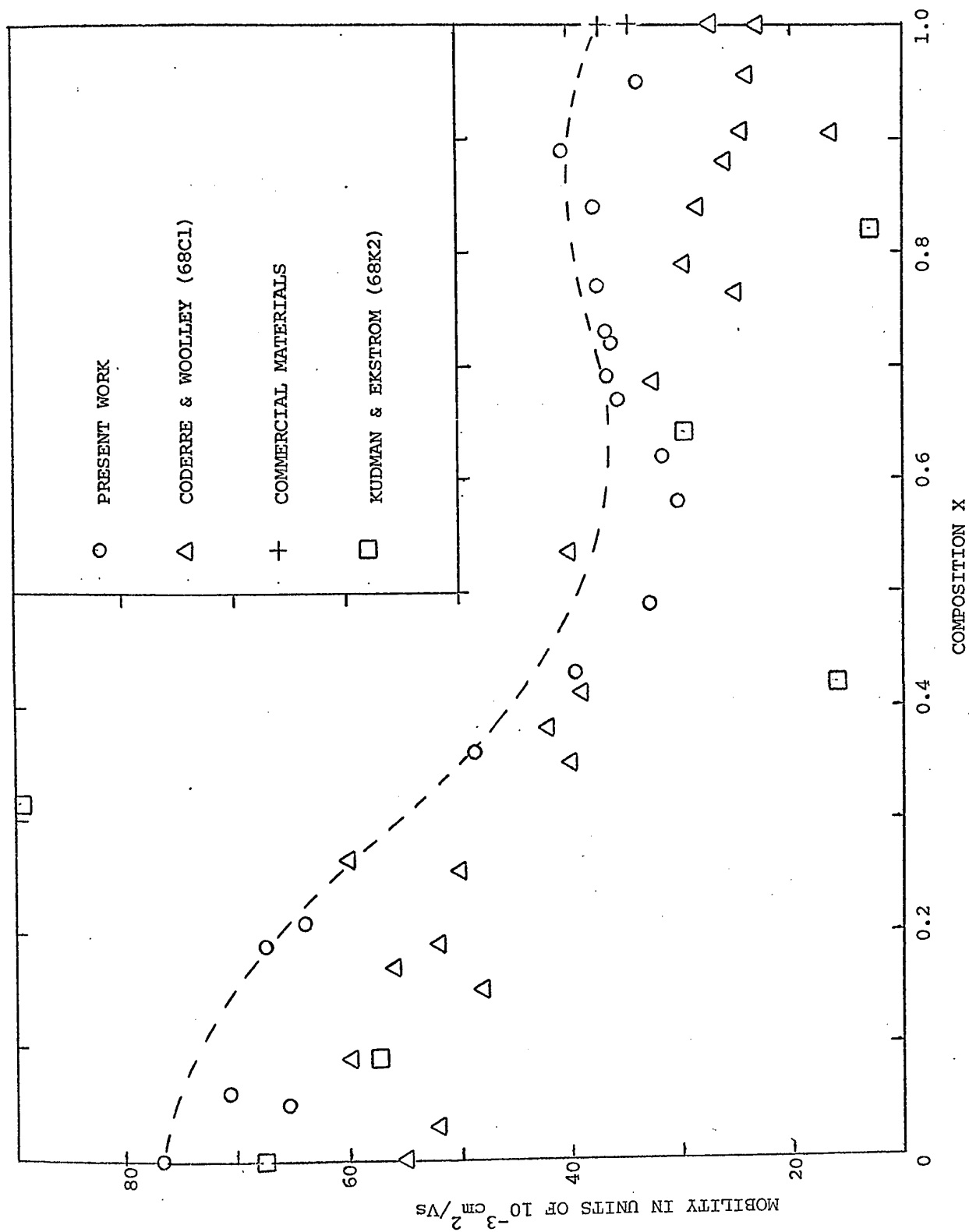
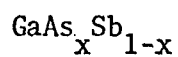


Figure 2.3.4. Experimental mobilities in $\text{InAs}_x\text{Sb}_{1-x}$

this suggests that the lattice parameter vs. composition data of Woolley and Warner (64W1) are valid, since the profile obtained by assuming a Vegard law yields an average composition of only 0.365.



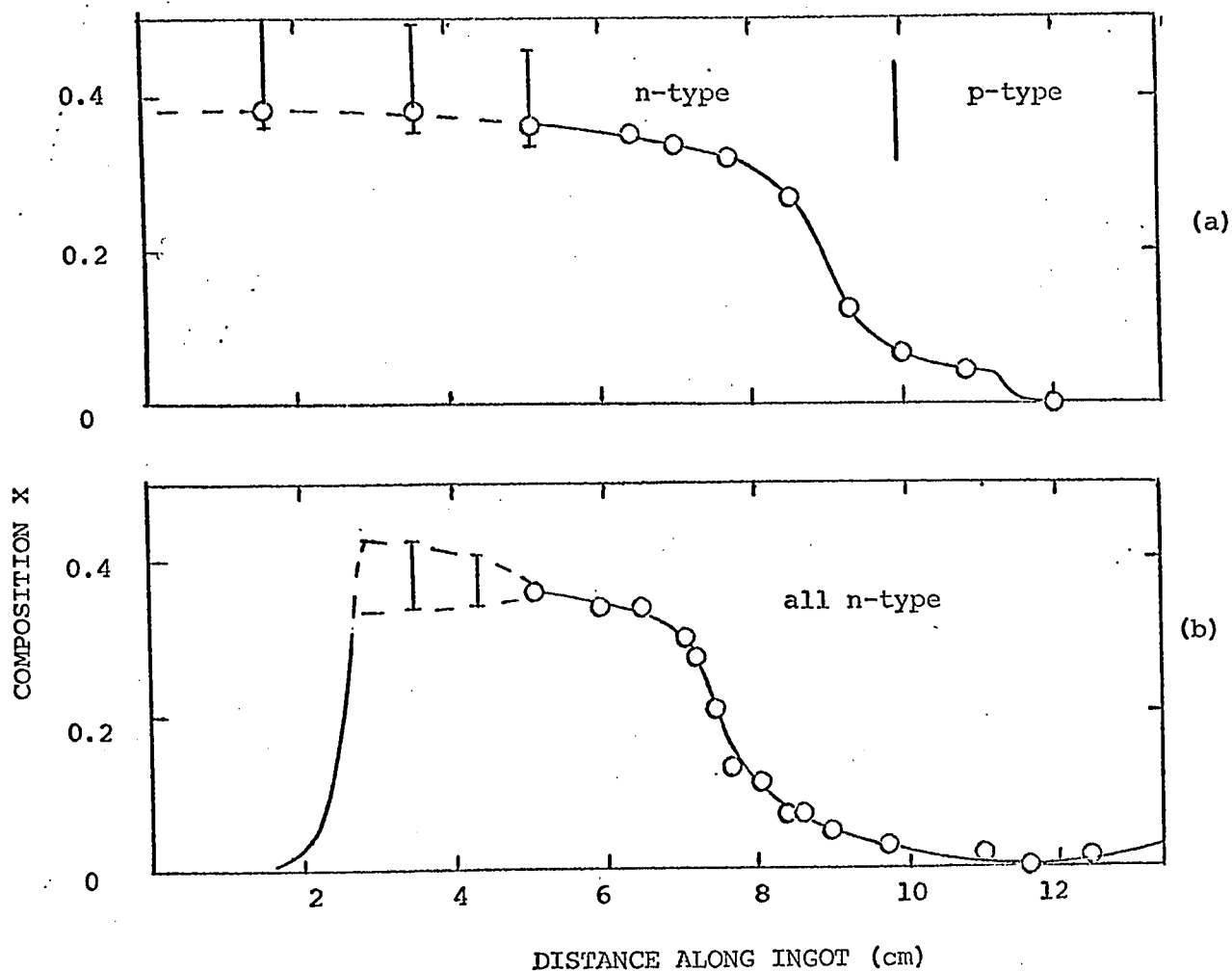
These ingots were prepared using zone furnace no. 2, which gave a zone length of 1 to 2 cm, and steeper temperature gradients, which were not measured because of experimental difficulties. Growth conditions for 4 ingots are summarized in Table 2.3.B

Table 2.3.B.

$\text{GaAs}_x\text{Sb}_{1-x}$ ingots

#	initial x	mass (g)	length (cm)	Te (mg)	nominal growth rates, (cm/day)		
					step-freeze	1st zone	2nd zone
TZF 3	0.3	31	14	—	79	0.27	—
TZF 4	0.3	31	13	1.2	198	0.92*	0.27
TZF 5	0.3	31	13	0.9	198	0.92	0.27
TZF 6	0.2	32	13	13.1	198	0.27	—

* mechanical drive was switched off several times, when liquid zone lagged seriously behind heater.

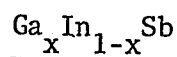


u	5.1	6.5	7.1	7.2	7.7	8.1	8.6	9.8	11.7	(cm)
n_H	24.	26.	24.	24.	15.	12.	10.	7.2	6.3	(units of 10^{17} cm^{-3})
μ_H	770	625	1800	1183	2400	2800	2760	2760	120	(cm^2/Vs)

Figure 2.3.5. GaAs_xSb_{1-x} ingot composition profiles: (a) TZF5, (b) TZF6. The table shows apparent electron density and mobility as a function of position u along ingot TZF6.

Following each step-freeze, an idea of the composition tapering was given by the external appearance of the ingot within its ampoule. Several other ingots were examined by lapping and examining the surface under low magnification. The GaAs-rich phases were clearly visible as greyish-violet dendrites up to several mm long, surrounded by the plain grey GaSb-rich material. Despite the increased speed of the step-freeze compared to that used for $\text{InAs}_x\text{Sb}_{1-x}$, a less gradual tapering was achieved, as shown in Fig. 2.3.5. Only the last ingot was n-type everywhere, including the GaSb-rich end. This was achieved by using several times more Te than would appear necessary, assuming segregation coefficients of 0.5 and 0.2 for the rapid step-freeze and slow zone growth respectively. It seems that Te was lost by condensation on the wall of the ampoule above the ingot, while adjacent to the water-cooling jacket on the growth side during the final zone pass. As mentioned in section 2.1, this could be overcome by suitable design of the jackets.

No theoretical profiles are shown for these ingots because the phase diagram remains too inaccurately known to warrant their inclusion.



Because of moderate segregation in this system, homogeneous ingots with tapered composition can be prepared by step-freezing alone, but sequential growth was found to be preferable for Te-doped material.

This gave polycrystalline ingots of large enough grain size that specimens could be chosen to exclude resistance barriers, as described in section 3.2. The results are summarized in Table 2.3.C.,

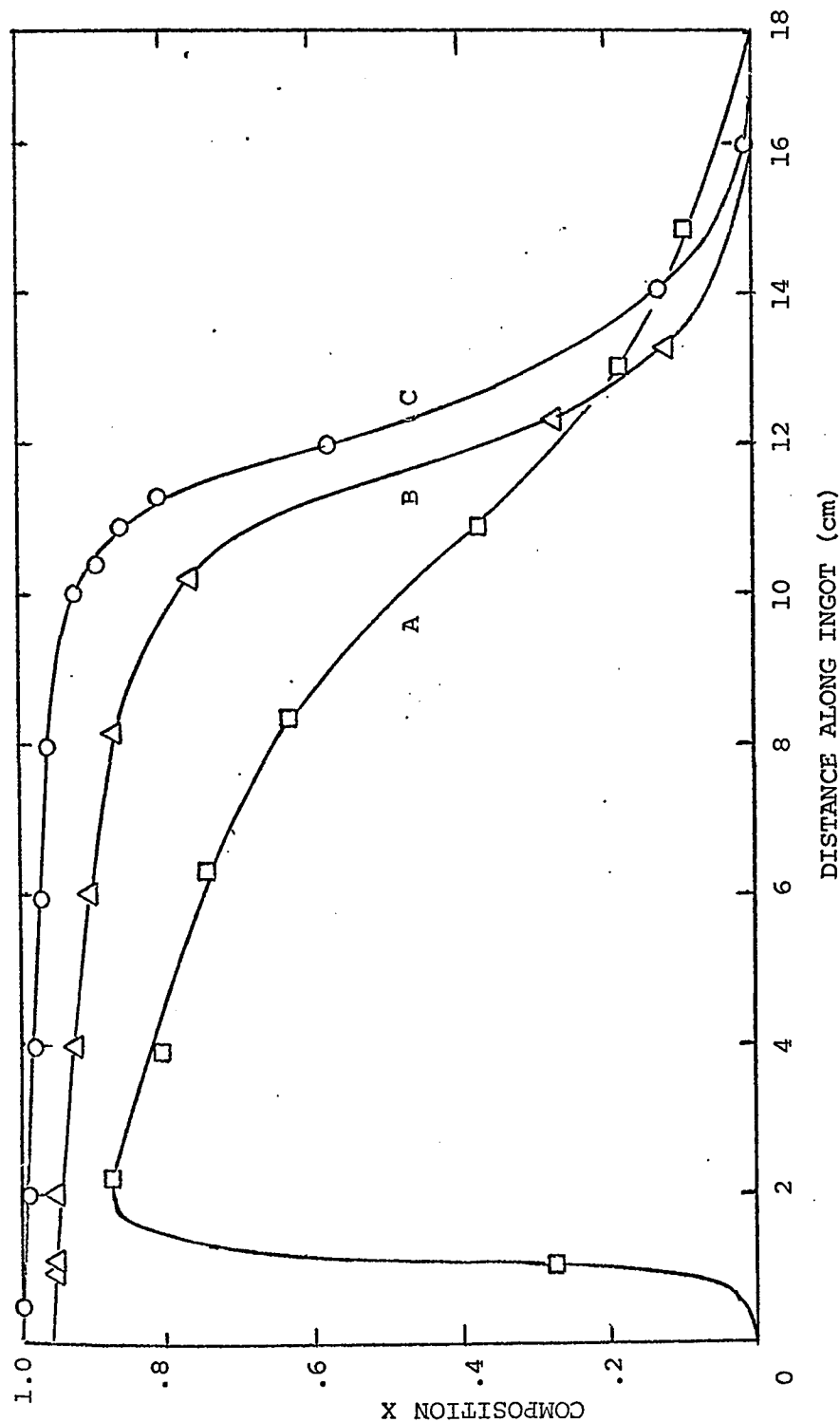
Table 2.3.C.

$$\text{Ga}_{1-x}\text{In}_x\text{Sb ingots}$$

* Reversed-zone sequential growth, with 0.7 mg extra Te

#	initial x	mass (g)	length (cm)	Te (mg)	nominal growth rates, (cm/day)		
					step-freeze	1st zone	2nd zone
TFA12	0.7	49	16.5	4.1	1.2	—	—
TZA2	0.5	48	17.5	1.6	1.2	1.8	—
TZA3	0.7	51	17.5	21.	1.2	0.6*	—

The first ingot was given only the step-freeze, the second was given ordinary sequential growth, and the third was given "reversed-zone sequential growth", meaning that the zone pass was commenced at the high-melting end. The purpose of using a reversed zone was to provide a composition profile tapering all the way down from almost-pure GaSb. The profiles are shown in Fig. 2.3.6, which also shows the carrier concentrations and mobilities at various points along ingot TZA3. At the time that ingot TZA2 was grown, the idea of using a reversed zone was not apparent. In fact it would have provided a more useful profile than the standard sequential process actually used. (The reversed-zone sequence caused no practical problems in this alloy system,



cm	0.5	2.0	4.0	8.0	10.	10.4	10.9	11.3	12.0	14.1	16.
n_H	0.335	0.42	0.37	0.68	0.89	1.07	1.32	1.78	2.95	5.5	7.7
μ_H	3390.	2330.	254.	4250.	5360.	5800.	5580.	7280.	2575.	4822.	5900.
										(cm^2/Vs)	
										(units of 10^{18} cm^{-3})	

Figure 2.3.6. Experimental composition profiles for $\text{GaIn}_{1-x}\text{Sb}$; A: ingot TZA2; B: ingot TFA12; C: ingot TZA3. The table shows apparent electron density and mobility along ingot TZA3;

since the liquidus temperature at the high-melting end was less than 730°C.) Since the step-freeze concentrates the Te-dopant towards the InSb-rich end the dopant should have been added immediately prior to the zone pass.

A Miscibility Gap in $\text{GaAs}_x\text{Sb}_{1-x}$?

Since the foregoing was written there have been several advances in knowledge of the system $\text{GaAs}_x\text{Sb}_{1-x}$. It was previously known that step-freeze profiles in this system were extremely steeply-graded, and it was possible to cut out samples showing an abrupt change of colour within less than 0.1 cm. M. Gratton of this group has recently shown by chemical staining of such samples that the change of colour appears abrupt even under high optical magnification. He also conducted measurements of lattice parameter by Debye-Scherrer methods as a function of composition determined by the back-scatter of radiation using an iodine radio-isotope source. He verified the Végard relation in all material studied, but the abrupt transition corresponded to a miscibility gap in the range $0.36 \leq x \leq 0.85$. Support for the view that this alloy system contains a miscibility gap then also came from calculations by Stringfellow (72S1) of the phase diagram of this system, which predicted a gap of similar magnitude but shifted to smaller values of x . The sequential growth ingots reported in the present work support the experimental observation of 0.36 as the lower limit. (The present work was not concerned with values

appreciably larger than this, the interest for pressure dependence being confined to GaSb-rich material.)

2.4 SUMMARY OF MATERIAL PREPARATION WORK

In section 2.1 the techniques of bulk growth from stoichiometric liquids have been discussed, with particular reference to the sequential growth technique which was developed by the author to provide smoothly-tapered composition profiles even when the alloy components are highly segregating.

In section 2.2 a set of rules was formulated for better understanding of growth techniques generally, and especially of sequential growth, which involves the simultaneous growth and dissolution of alloys under conditions of imperfect mixing. Some of these rules are well known, and the stagnant-layer model for imperfect mixing was copied from the work of others, but the quantitative statement of rules governing the dissolution interface is only vaguely implied in prior work.

Also described in section 2.2 was the application of the growth rules to the computer prediction of composition profiles along ingots. After successful comparison with some experimental results of other workers the computer prediction was applied to assist in the choice of suitable conditions for sequential growth.

In section 2.3 the experimental results of the material preparation work were given, and it was noted that the computer-predicted profiles for sequential growth differed appreciably from those actually found. It appears that the stagnant layer model as formulated becomes inadequate when the mixing is highly imperfect, as during rapid step-freezing of highly-segregating alloys. Even so, the computer predictions gave useful guidance for the slow and painstaking work of growing ingots.

3. SPECIMENS AND APPARATUS

3.1 PRINCIPLES

Van der Pauw Method

In the method of Van der Pauw (58P1), the specimen has four contacts, which are best located symmetrically, and the resistivity ρ is given by

$$\exp(-\pi R_1 d / \rho) + \exp(-\pi R_2 d / \rho) = 1 \quad 3.1.1$$

where d is the thickness of the sample, assumed parallel. R_1 is the four-terminal resistance, the current being applied through a pair of adjacent contacts, and the potential being measured on the remaining pair. R_2 is the resistance obtained by permuting all the contacts cyclically by one position. It is convenient to define a function K such that

$$\rho = 4.532 K R_2 d \quad 3.1.2$$

For an almost symmetrical geometry it can be shown that

$$K \approx (R_1 / R_2)^{1/2} \quad 3.1.3$$

The Hall coefficient is given by

$$R_H = \Delta R d / B \times 10^{-5} \quad 3.1.4$$

where ΔR is the change due to applying the magnetic field, in the resistance obtained by passing current between one pair of opposing contacts, and measuring potential on the other pair. Usually the field is reversed, which yields $2\Delta R$. The numerical factor applies if ΔR and d

are expressed in cm units, and B in kilogauss, and yields R_H in $\text{cm}^3 \text{C}^{-1}$.

Apparent Carrier Concentration and Mobility

These quantities are convenient for approximate evaluations as in section 2.3; by definition,

$$n_H = 1/eR_H \quad 3.1.5$$

$$\mu_H = 1/en_H \rho \quad 3.1.6$$

μ_H is often called the Hall mobility.

Correction For Dimensional Compression

This effect is small and quite unimportant in most cases, but will be included in the discussion concerning the possibility of two-band conduction in heavily-doped InAs. When isotropic pressure is applied, the specimen decreases in volume by about 2% at 12 Kb. Specifically, the thickness decreases in the ratio

$$d/d_0 \approx 1 - \frac{1}{3} K_V P \quad 3.1.7$$

where K_V is the volume compressibility. The Hall coefficient then varies as

$$R_H/R_{H0} \approx (\Delta V_H/V_{H0}) (1 - \frac{1}{3} K_V P) \quad 3.1.8$$

providing the current and magnetic field do not change. However, the impurity and related densities increase in the ratio

$$N/N_0 \approx 1 + K_V P \quad 3.1.9$$

since the number per unit cell remains constant. In single-band conduction, with a constant total number of carriers and unity value of the averaging parameter (section 4.3), eq. 3.1.5 gives the true value of the carrier concentration. Since the pressure variation of Hall effect is usually recorded as $\Delta V_H / \Delta V_{H_0}$, this uncorrected ratio should vary with pressure as:

$$\Delta V_H / \Delta V_{H_0} = \frac{1}{(1 + K_V P) (1 - \frac{1}{3} K_V P)} \quad 3.1.10$$

Some experimental (60B1) and theoretical (71C1) values of K_V are given in Table 3.1.A.

Table 3.1.A

Volume compressibilities K_V , (units are 10^{-3} Kb^{-1})

	Si	Ge	GaAs	GaSb	InAs	InSb
experimental	1.038	1.36	—	1.80	—	3.04
theoretical	1.02	1.33	1.34	1.77	1.72	2.2

3.2 SPECIMENS

Preparation

The specimens were squares of about 0.3 x 0.3 cm size, cut from ingot cross-sections about .06 cm in thickness. All cutting was done with a spark cutter built in our machine shop to a design of the National Research Council. The broad surfaces were hand-lapped with 5-micron

abrasive and water on glass plates. The sides were not lapped, and no etching was attempted, since this is difficult on alloys, (often requiring a different formula for each composition). In any case, it seemed clear that surface effects would be small compared to bulk effects in these specimens. Gold wires of .005 inches diameter were attached to each corner of the squares by Aremco Bond 525 conductive epoxy cement², which was then cured by heating the specimens at about 270°C for 10 minutes in air. Typically, the conductive cement contacts were about .03 cm across, and because of the current flow patterns in a square geometry, this size was adequately small to approximate the ideal Van der Pauw theory.

Resistance Barriers in Te-doped Ingots

When specimens were first cut from Te-doped, GaSb-rich ingots, they were frequently asymmetric in apparent resistance, when the contacts were permuted as in the Van der Pauw technique. Asymmetries up to 1:1.5 could be due to deviation from the perfect square geometry with corner contacts; this was verified by constructing models from filter paper soaked in an electrolyte, but this could not explain ratios up to 1:7 which were found in the early measurements. The possibility of large variations in carrier concentration was at first investigated by measurement of spreading resistance (66M1) using a tungsten-carbide probe with a fine point of about 10 microns radius, which was spring-loaded against the lapped surface. The probe was positioned using a 3-dimensional micrometer, and the spring compression could be accurately reproduced by means

of an electrical make/break contact which was attached to it. Unfortunately, as already mentioned, the surfaces could not be etched. The observed variations of about a factor of two did not correlate with the 4-terminal asymmetries.

The problem was solved for practical purposes by using the same probing apparatus in a different mode: a current was passed between pressure contacts applied to the edges of specimens (consisting usually of complete ingot cross-sections), and the probe was used to explore the potential distribution on the surface. All the Te-doped, GaSb-rich material contained sharp discontinuities of potential at grain boundaries. Fig. 3.2.1 (a), (b) show examples of such behaviour, compared in Fig. 3.2.1 (c) to an undoped specimen of $\text{InAs}_x\text{Sb}_{1-x}$ showing regular behaviour. Attempts to resolve the potential discontinuities by dragging the needle were unsuccessful; the jumps in voltmeter reading were apparently instantaneous. The amplitude and sign of the jumps were found to be proportional to the current; therefore they will be called "resistance barriers". Some $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ material was found to be almost single-crystal over the cross-sectional area, except for twin boundaries, which can be easily recognized since they usually appear as sets of two or more parallel planes. No discontinuities could be found across twin boundaries.

It was found that the presence of barriers could be easily revealed in lightly-doped material ($n < 10^{18} \text{ cm}^{-3}$) by putting a drop of acidified copper sulphate solution on the surface, and then applying a potential of 1.5 volts for a few seconds between two points on the periphery. The resulting copper deposit tapered up to a maximum on the cathodic side of each barrier, where it terminated abruptly.

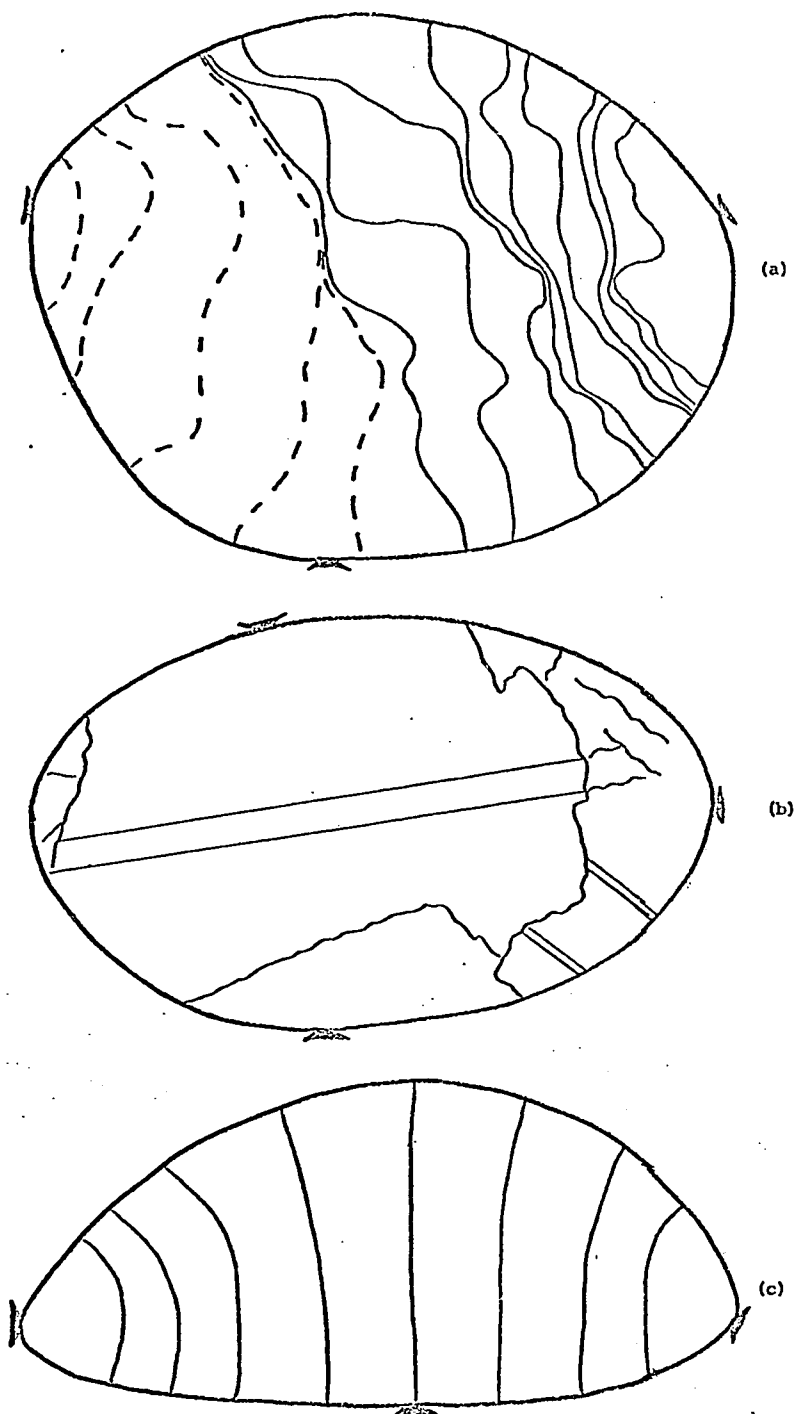


Figure 3.2.1. Potential maps on cross-sections of ingots, showing the presence of resistance barriers in the case of Te-doped, GaSb-rich alloys.

- (a) $\text{GaAs}_{0.24}\text{Sb}_{0.76}$: smooth contours show 10. mV intervals; dotted contours at 0.02 mV intervals show that part of cross-section is almost free from barriers.
- (b) $\text{Ga}_{0.96}\text{In}_{0.04}\text{Sb}$: curved lines show irregular grain boundaries with potential discontinuities; straight lines (twin boundaries) are visible but show no potential discontinuities.
- (c) undoped $\text{InAs}_{0.72}\text{Sb}_{0.28}$ shows smooth contours everywhere.

Selection of Specimens

Once the nature of the asymmetries was established, all specimens from Te-doped, GaSb-rich ingots were selected in the following way. Four pressure contacts were applied around the periphery of each cross-sectional slice, and the apparent resistivity and Hall coefficient measured, then the potential distribution was examined as described. One or more square regions were selected as being apparently free from barriers, and marked by dragging the needle around the selected periphery, meanwhile observing the voltmeter for sudden jumps. Specimens selected in this way were symmetrical to within 1:1.5. in most cases, in the ratio R_1/R_2 .*

Cut specimens were tested in a holder which applied pressure contacts to each of the four corners, the better specimens being selected for assembly with epoxy contacts and gold wires.

Further Comments on Barriers

It seems likely that little current actually crosses the barriers, but finds alternative paths instead. This would explain the occurrence of high asymmetries, greater than 1:10, and in one case, 1:150 which were found in specimens cut at random. Frequently, when a whole cross-section was measured as described, there was little asymmetry, but a much higher resistivity than obtained later when a selected specimen was cut from it. On the other hand, randomly-cut specimens were highly asymmetric. This indicates a tendency for barriers to terminate upon themselves or upon

* Not all the specimens were selected in this way, but even so, meaningful results can be deduced from the pressure data, as discussed in Sections 5.2 and 6.2.

each other, rather than at the ingot surface. The possibility of 3-dimensional current paths, and the internal termination of barriers in such a way as to isolate some areas completely, are violations of the conditions assumed in the Van der Pauw analysis, and correct resistivity readings cannot be expected.

Compared with the serious interference caused by barriers in the resistivity measurements, the measured Hall coefficient is virtually independent of them. On one cross-section having composition $\text{Ga}_{.96}\text{In}_{.04}\text{Sb}$, the apparent resistivity was 0.167 ohm-cm, but only .0018 ohm-cm on the specimen selected from it. In contrast, the Hall coefficient changed only slightly, from 6.3 to 7.4, so the selected specimen indicated one hundred times higher mobility. The invariance in Hall coefficient might be explained by some generalization of the Van der Pauw analysis.

3.3. APPARATUS

Electrical Measurements.

The specimen current was supplied by a battery-operated, current-regulated source, and potentials were measured on a Keithley model 155 battery-operated D.C. microvoltmeter. The current through the specimen and standardizing resistor (in series) was reversed at 10 c.p.s. by a low-thermal mechanical chopping switch, which also reversed the voltmeter connections synchronously. The voltmeter was used for both current and voltage measurements, by means of a manual switch, and this electrical system was used in all the potential probing work. All six permutations

of the specimen contacts could be selected, 4 of these being for resistivity measurement, and 2 for Hall effect. The magnet was a Newport Instruments unit, with Harvey Wells HS1020 power supply.

Calibration was done using a rotating coil gaussmeter, which had been standardized against a nuclear resonance instrument. For all pressure runs, a field of 5.1 kilogauss was used; for preliminary measurements on ingot cross-sections and square specimens, additional pole-pieces were attached, which raised the field to 8.0 kilogauss.

High Pressure

The pressure system was of the intensifier type, constructed from commercial components except for the pressure vessel in which the specimens were measured, and the manganin high pressure gauge. As shown in Fig. 3.3.1, a motor-driven pump and pressure reservoir delivered hydraulic oil to the Harwood Engineering Company³ A2.5J intensifier, giving a 16-fold nominal intensification of pressure, with a rated output of 13.6 Kb. The high pressure fluid (naphtha) was conveyed by non-magnetic capillary tubing (56Pl) to the beryllium copper pressure vessel. All high pressure elements were shielded by 3/8-inch steel plates, and a relief valve was fitted on the primary pressure side to prevent overloading. In practice, 13.6 Kb was never quite reached, due to leaks on the high pressure side at the tubing unions (glands). After releasing pressure, the intensifier was returned completely to its starting point, using a manual pump on the high pressure side; this pump was also used to remove the plug carrying

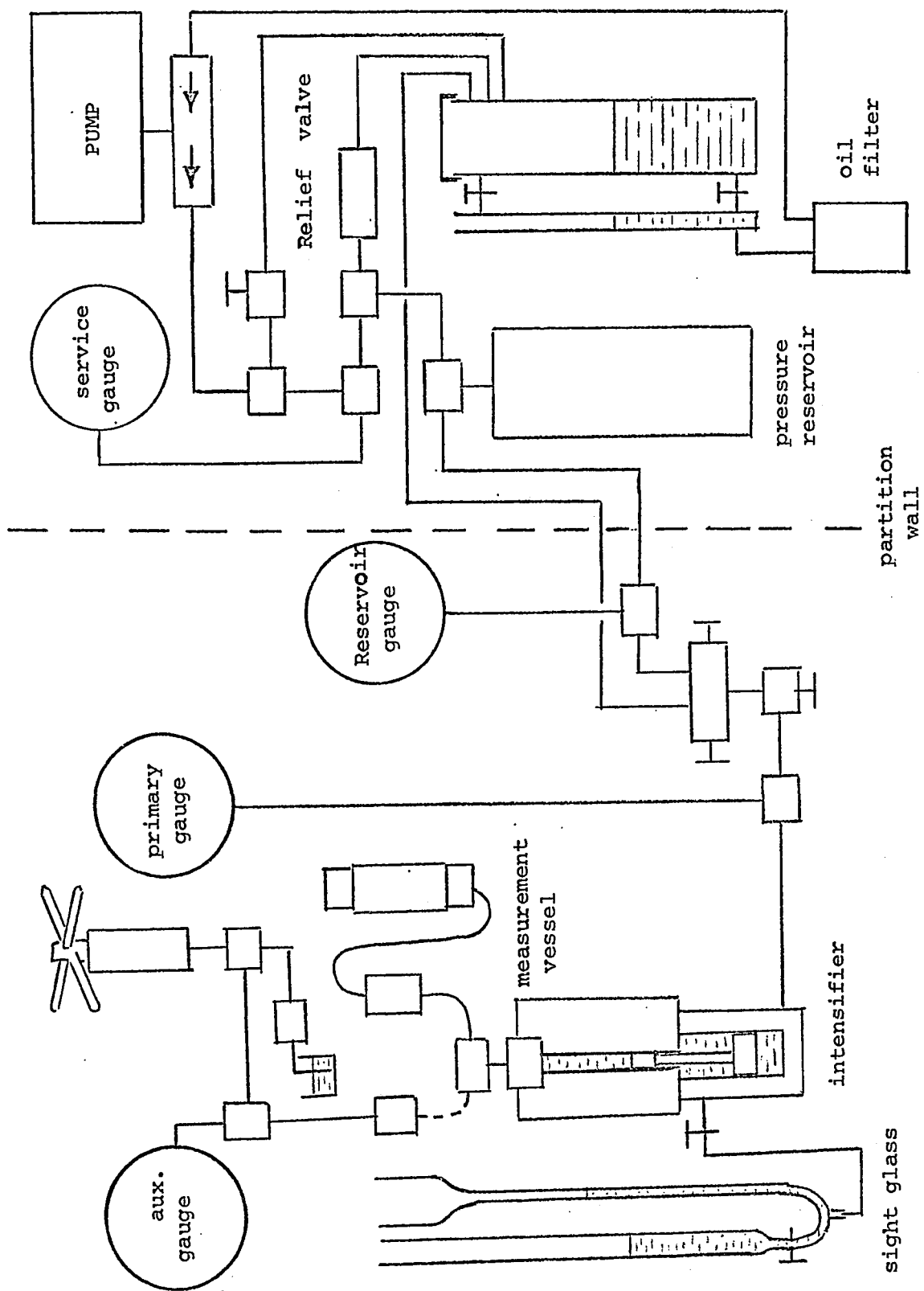


Figure 3.3.1. Schematic diagram of high pressure system.

the specimen. During pressure operation, the manual pump connection was replaced by a blank plug.

Fig. 3.3.2 shows the pressure vessel, which was constructed in our machine shop. The cylinder and end plugs were beryllium copper, hardened to Rockwell C40 after machining (59P1). Other parts were non-magnetic stainless steel. The construction of the fluid inlet plug is shown inset in the figure, with its sealing rings: a stainless steel wedge ring, a backup ring, and conventional rubber O-ring. Various materials were used for the backup ring; lead, teflon, delryn and indium-plated copper. Eventually it was found that a more reliable seal was obtained with no backup ring. The seals were thickly coated with silicone grease before use, since this was found to reduce the residual leakage. Electrical connections were brought into the pressurized system through swaged thermocouple tubing, (61C1) of 0.04 inches diameter, obtained from Thermo Electric Corporation⁴. Four pieces of this tubing were silver soldered into a threaded hole in a stainless steel cone, which was soft soldered into the beryllium copper plug. Initially, epoxy cement was used, but the joint became leaky after about 25 pressure cycles, due probably to uneven distortion between the stainless steel and the beryllium copper. This arrangement provided four copper wires for connections to the specimen, and two of the four constantan wires were used for connections to the manganin gauge.

This gauge was wound from 40 SWG enamelled manganin wire, yielding a resistance of 1500 ohms, so that calibration was not appreciably dependent on the constantan wires, since these had an overall resistance of only 5 ohms. The gauge resistance increased by about 35 ohms at 12 Kb, and this was measured on a bridge which was designed to expand the pressure

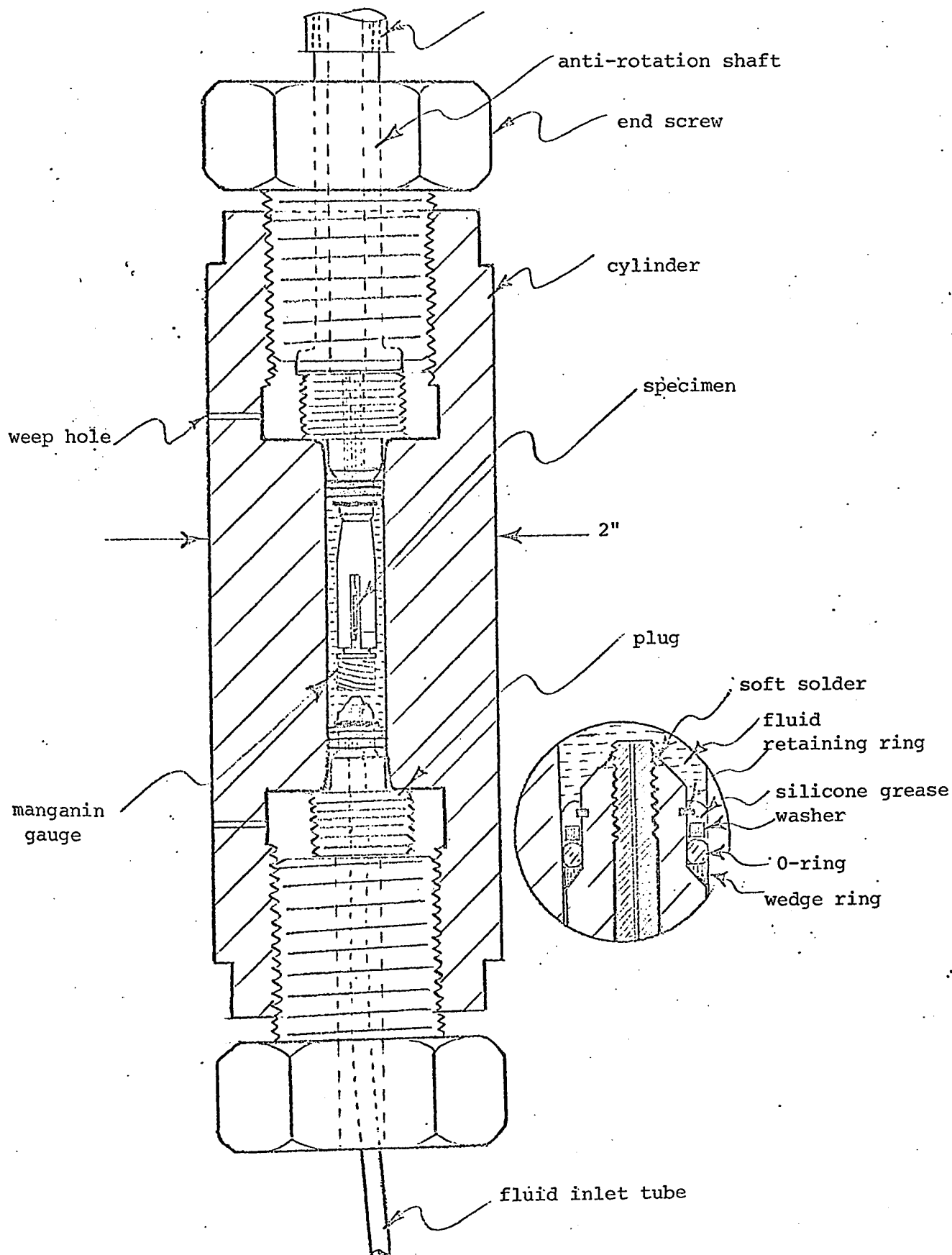


Figure 3.3.2. High pressure measurement vessel, with inset showing structure of pressure seals.

scale over many turns of a helical potentiometer, as in Fig. 3.3.3. After about 25 measurement runs the gauge developed short circuits and had to be replaced. Bridgman (52B1) recommended silk-covered wire, but this is more bulky.

Pressure calibration was performed by connecting a bourdon-type gauge to the system. The calibration gauge was connected to the high pressure side of the system, at the point (see Fig. 3.3.1) where the manual pump was connected for returning the intensifier to its starting position. This gauge was loaned to us by the National Research Council, and had been standardized by them using the ice V/VI/ liquid triple point, combined with a differential mercury column technique. The manganin gauge proved to be within 0.1% of linear up to the bourdon gauge limit of 7 Kb; beyond this the calibration was deduced by extrapolation. The pressure coefficient of the gauge was determined as $2.33 \times 10^{-3} \text{ Kb}^{-1}$, which is within the range established by Bridgman (52B1).

Pressure values may be converted into other units using the following factors:

$$1 \text{ Kb} = 1000 \text{ atm.} = 1035. \text{ Kg/cm}^2 = 14,700 \text{ p.s.i.} \quad 3.3.1$$

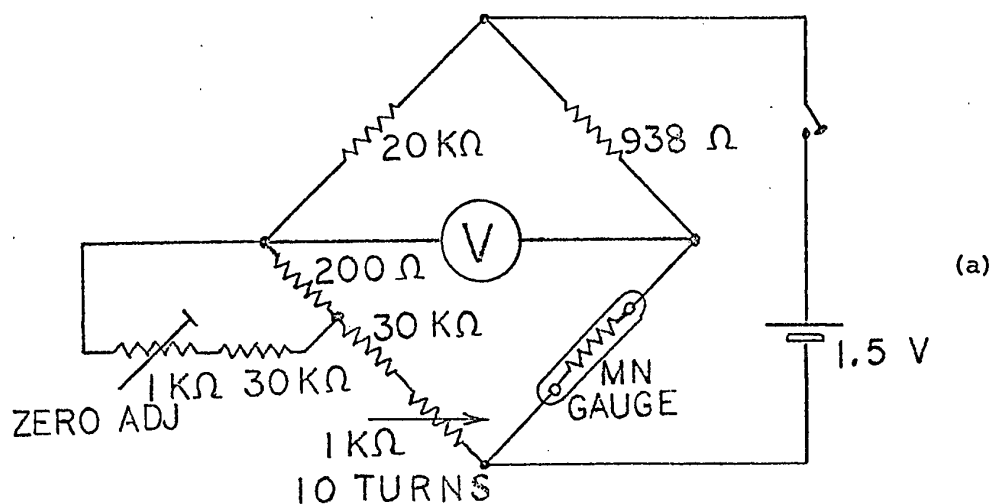


Figure 3.3.3. (a) Measuring bridge for manganin pressure gauge having a resistance of 1412 ohms at low pressure.

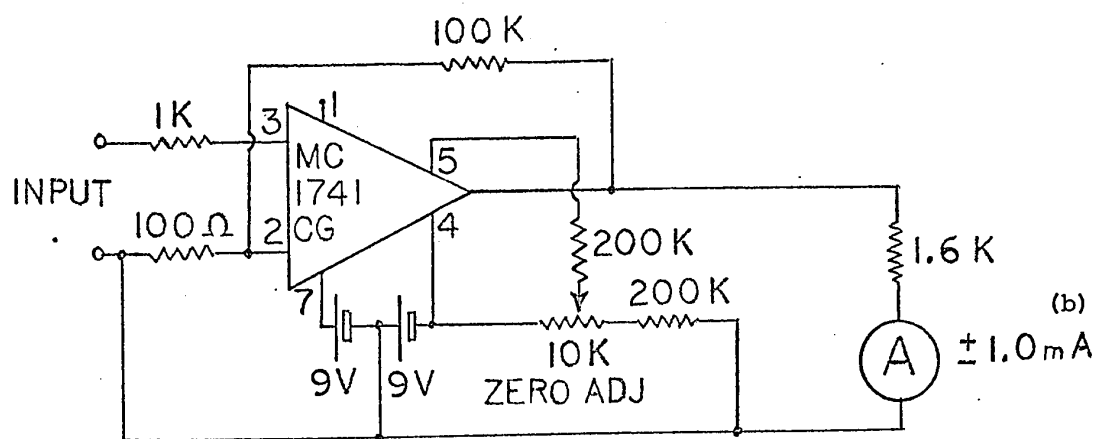


Figure 3.3.3. (b) null indicator "v" constructed around an integrated amplifier, with gain adjusted so that ± 1 Kb off-balance gave full-scale deflection on the milliammeter.

4. THEORY RELATING TO TRANSPORT

4.1 BAND STRUCTURE AND PARAMETERS

Scope

In this section some relevant standard material will be summarized, with special attention to certain aspects where misunderstanding can easily occur, as for example in the definition of effective mass, and in the assumption of full ionization of impurities in heavily-doped semiconductors.

In addition, the variation of effective mass m^* with pressure will be deduced empirically by showing that the experimental variation of m^* with band-gap E_G for varying alloy composition resembles the variation of m^* with E_G which is predicted by assuming that the parameters E_p and Δ_0 of the Kane model remain constant as E_G varies with pressure or composition. The only prior discussion of this point seems to have been that of Ehrenreich (57E1) on InSb, for which the approximation $\Delta_0 \gg E_G$ is valid in the pressure range 0 - 2 Kb for which experimental results were available.

Effective Mass

For transport under elastic scattering in non-parabolic but spherically-symmetric bands, the effective mass should be defined, according to Kolodziejczak (61K1), Zawadski and Szymanska (71Z1) and others, as

$$m^*(E) = \hbar^2 k / \frac{dE}{dk} \quad .4.1.1$$

where E is the energy corresponding to wave vector k in the band. Some earlier authors had recognized this implicitly, while retaining the name "effective mass" for the "band curvature mass" defined as $\hbar^2 / \frac{d^2 E}{dk^2}$, which reduces to eq. 4.1.1 in the parabolic case only. Barrie (56B1), Sosnowski (64S1) as well as the above found that the band curvature mass (which determines the acceleration, see e.g. Smith, 59S1, p. 38) splits into two parts in the Boltzmann transport equation; the first gives the same contribution as eq. 4.1.1, while the second part vanishes when the scattering is elastic, as assumed here. In simpler language, the Boltzmann equation for elastic scattering involves velocity but not acceleration, and the relation between velocity and momentum $\hbar k$ is eq. 4.1.1. This "momentum mass" also allows the expression of many equations in familiar forms, as originally derived for parabolic bands.

Kane Model

According to Kane, (57K1) the shape of the conduction band near $k = 0$ is given by one of the four solutions of the equations

$$E' [E' (E' - E_G) (E' + \Delta_0) - k^2 \frac{\hbar^2}{2m} E_p (E' + 2\Delta_0/3)] = 0 \quad 4.1.2$$

where E' is the energy E minus the free-electron energy:

$$E' = E - k^2 \hbar^2 / 2m \quad 4.1.3$$

and E_G , Δ_0 are the band gap and the valence band spin-orbit splitting respectively at $k = 0$. The energy parameter E_p may be calculated from experimental values of E_G , Δ_0 and m_0^* the effective mass at $k = 0$,

by combining eqs. 4.1.1 and 4.1.2 to form the relation

$$m/m_o^* = 1 + E_p(E_G + 2\Delta_o/3)/E_G(E_G + \Delta_o) \quad 4.1.4$$

E_p is close to 20 eV in the compounds of present interest, (64M1, p. 357) and in some at least of their alloys, (72B2). Aubin and Woolley (68A1) derived the following approximations to eq. 4.1.2, in which both E and k are expressed explicitly in terms of the other, and in terms of m_o^* in place of Δ_o and E_p :

$$E(k) = \alpha k^2 + \frac{1}{2} E_G \left[\{1 + 4\alpha k^2 (m/m_o^* - 1)/E_G\}^{1/2} - 1 \right] \quad 4.1.5$$

$$k(E) = \left(\frac{E_G m}{2\alpha m_o^*} \right)^{1/2} \left[1 + \frac{2Em_o^*}{E_G m} - \left\{ 1 + \frac{4Em_o^*}{E_G m} (1 - m_o^*/m) \right\}^{1/2} \right]^{1/2} \quad 4.1.6$$

where $\alpha = \hbar^2/2m$. Here, the origin of E has been shifted from the top of the valence band to the bottom of the conduction band. To the same approximation, the effective mass is given by

$$\frac{m}{m^*(k)} = 1 + \left(\frac{m}{m_o^*} - 1 \right) / \left\{ 1 + 4\alpha \left(\frac{m}{m_o^*} - 1 \right) k^2/E_G \right\}^{1/2} \quad 4.1.7$$

A comparison between eqs. 4.1.2 and 4.1.6 is shown in Fig. 4.1.1 for several III-V compounds, using Δ_o as listed by Cardona (69C1), and with E_p obtained from eq. 4.1.4. The more approximate form is adequate for electron concentrations up to about 10^{18} cm^{-3} in the <ooo> band, for which the range of k up to $5 \times 10^8 \text{ m}^{-1}$ is important. The discrepancies may fall within the error due to neglect of higher-band interactions in the basic Kane theory; inclusion of these brings in deviations from

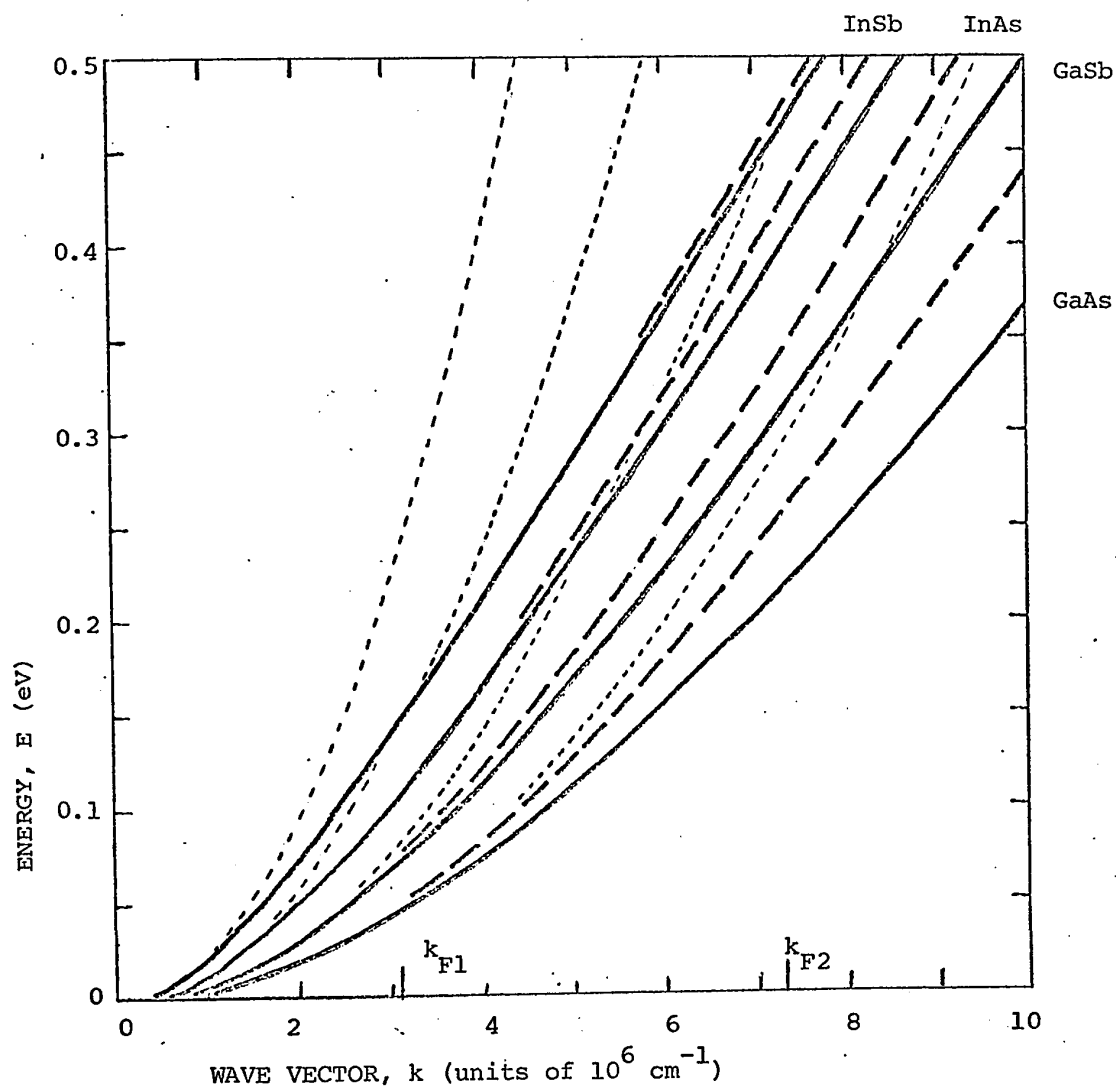


Figure 4.1.1 Conduction band shapes in III-V compounds near $k = 0$.

Smooth curves: basic Kane model; dashed curves: from equation 4.1.5, (68A1); dotted curves: parabolas fitted to bottom of bands. The Fermi radii k_{F1} and k_{F2} respectively enclose 10^{18} and 10^{19} cm^{-3} electron states.

spherical symmetry, which requires more sophistication than could be justified for the present transport data on alloys.

Impurity States

According to the hydrogenic model of shallow impurity states, the bound-electron wave functions extend over a large number of host atoms, and a quasi-Bohr theory can be used. The binding energy of an impurity state is then given in terms of the bulk dielectric constant, $\kappa\epsilon_0$ as

$$E_D = 13.5 \, m^*/m\kappa^2 \, \text{eV} \quad 4.1.8$$

where m^* refers to the band from which the impurity state is derived. The state is then localized only to within the effective Bohr radius defined by

$$a^* = 0.53 \, m\kappa/m^* \, \text{\AA} \quad 4.1.9$$

By the uncertainty principle, the state cannot be localized in k -space to closer than an amount δk , given by

$$a^* \, \delta k \sim 1 \quad 4.1.10$$

Shallow states have small values of E_D and large values of a^* , (10 to 100 lattice spacings), so that localization within the Brillouin zone is not forbidden. The existence of localized states is well established,

but evidence shows that in general an impurity state is associated with all the significant band minima in varying degrees. The binding energy relative to each minimum depends on the respective effective masses, but is perturbed by the proximity (in energy) of other bands, and this also affects the relative probability of each association, (66K1), (71A1). This complicates the calculation of impurity ionization in multiband materials under varying temperature and pressure. However, when the carrier concentration exceeds 10^{17} cm^{-3} , as in the GaSb-rich alloys, the screening radius (see section 4.2) shrinks to the order of a^* or less. For such screened-Coulomb potentials no bound states exist, and the impurities must be fully ionized, (64Z1, p. 145). A contributory reason for assuming full ionization when the impurities are close together, is the merging of states into the band due to resonance broadening, in which case these states become part of the band.

III-V Alloys

It is well established that the four compounds GaAs, GaSb, InAs, InSb form pseudo-binary alloys with a direct band gap at the centre of the Brillouin zone in all cases. In the vicinity of $k = 0$ the conduction band is strongly curved (small effective mass) and spherically-symmetric, but non-parabolic. Additional conduction band minima have been observed or can be assumed to occur at the zone boundaries in the $\langle 111 \rangle$ directions, and at or near the boundaries in the $\langle 100 \rangle$ directions. The four $\langle 111 \rangle$ minima are especially prominent in GaSb, where they lie only about 0.087 eV

above the <000> minimum at room temperature and pressure, and measurement of this energy in GaSb-rich alloys was a principal object of this research.

Finite Temperature and Pressure

For several alloy systems, including $\text{Ga}_x\text{In}_{1-x}\text{Sb}$, the band gaps and their temperature dependences have been determined by Coderre and Woolley (68C1), (69C4), (70C1) from transport measurements. In $\text{GaAs}_x\text{Sb}_{1-x}$ the band gap as a function of composition has been determined by Thomas, Coderre and Woolley (70T2) from optical absorption data. They found non-linear variations with composition which could be accurately fitted by adding a parabolic (bowing) term to each otherwise linear variation. At room temperature and pressure the band gaps in $\text{GaAs}_x\text{Sb}_{1-x}$ and $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ can thus be expressed by

$$E_G = 0.725 - 0.51x + 1.2x^2 \quad 4.1.11$$

and

$$E_G = 0.175 + 0.13x + 0.42x^2$$

respectively.

The temperature dependences were expressed in the form proposed by Varshni (67V1):

$$E_G(T) = E_G(0) + \beta T^2 / (0 + T)$$

To facilitate the numerical analysis of the present data (Section 6) the following empirical relations were found to fit the data of Coderre and

Woolley in the case of $\text{Ga}_x\text{In}_{1-x}\text{Sb}$:

$$\beta = -6.3 \times 10^{-4} (E_G(300)/0.725)^{0.42} \text{ eV/}^\circ\text{K} \quad 4.1.12(a)$$

$$\theta = 265 (E_G(300)/0.725)^{0.21} \text{ }^\circ\text{K}$$

The temperature dependence in the case of $\text{GaAs}_x\text{Sb}_{1-x}$ has not been determined, but since the values of β are almost equal in GaAs and GaSb it was assumed that β was invariant with composition; θ was assumed to vary as a power of the band gap, determined to fit the known values in the compounds. Thus,

$$\beta = -6.3 \times 10^{-4} \quad 4.1.12(b)$$

$$\theta = 265 (E_G(300)/0.725)^{0.43}$$

Concerning pressure dependence, (relative to the valence band) it is well known that $\langle 000 \rangle$, $\langle 111 \rangle$ and $\langle 100 \rangle$ band extrema show characteristic shifts with isotropic pressure, which do not vary greatly from one group IV or III-V semiconductor to another; a summary of experimental values for many semiconductors has been prepared by Camphausen et al (71Cl) and compared with theoretically calculated values. In most cases, the agreement is good, although it should be noted that widely-differing values of the main-gap coefficient in InAs were obtained by earlier workers. However, the value of this coefficient is not of great importance in the present work. Table 4.1.A lists the values which were selected from (71Cl) for the compounds of present interest.

Table 4.1.A

Pressure coefficients

Pressure dependences of the $\langle 000 \rangle$ and $\langle 111 \rangle$ conduction band minima, relative to valence band maximum, averaged from ref. (71C1). Values in parentheses are purely theoretical. Units are meV/Kb.

material	$\langle 000 \rangle$	$\langle 111 \rangle$
GaAs	11.2	(2.8)
GaSb	14.7	5.0
InAs	10.2	(6.0)
InSb	16.5	(5.5)

For the alloys, linearly-interpolated values were used, and it will be seen that the experimental results indicate this assumption to be valid.

Concerning now the band curvature, the validity of the Kane model at finite temperatures is questionable in principle, since the band gap parameters include both lattice expansion and electron-phonon contributions. Ehrenreich (57E1) proposed an effective band gap parameter E_G^* which omits the electron-phonon interaction on the grounds that it does not affect the band curvature, but the analysis of Ravich (65R1) does not support this. Optical measurements on effective masses indicate that setting $E_G^*(T) = E_G(T)$ is a good approximation in InAs (67S1). The exact value of E_G^* is relatively unimportant to the pressure analysis at constant temperature, and the assumption of Aubin et al (69A1) was

followed uncritically:

$$E_G^*(T) = E_G(o) + \frac{1}{2} \{E_G(T) - E_G(o)\} \quad 4.1.13$$

When pressure P is applied at finite temperature, the thermal and pressure effects on lattice parameter will be additive if they are independent, which is to be expected only for small total changes in lattice parameter. The non-linearity in thermal dilation at low temperatures (67V1) may be relevant to this. For room-temperature calculations it should be safe to assume that E_G^* (no matter how it is determined) varies with pressure in the same way as E_G ; that is,

$$E_G^*(T,P) = E_G^*(T,o) + P (\partial E_G / \partial P)_T \quad 4.1.14$$

In order to apply eqs. 4.1.5 to 4.1.7 at finite temperatures and pressures the behaviour of m_o^* as well as E_G^* is required. Ehrenreich (57E1) assumed that with varying temperatures, and pressures up to 2 Kb, m_o^* varied proportionally to E_G^* in InSb; here, with pressures up to 12 Kb in various alloys a reappraisal was necessary. To deduce the variation of m_o^* with pressure we may note that in several III-V compounds and their alloys, m_o^* and E_G^* are in close correspondence. Fig. 4.1.2(a) shows experimental room temperature values of m_o^* and E_G^* in four III-V compounds and two of their alloy systems, taken from work by Aubin, Thomas, Van Tongerloo and Woolley, (68A1), (68T1), (69A1). For lack of space, the points shown in the figure are limited to those from (69A1) only. The straight line shown through the points in this figure led to the following assumed equation for m_o^* in all specimens, at all temperature

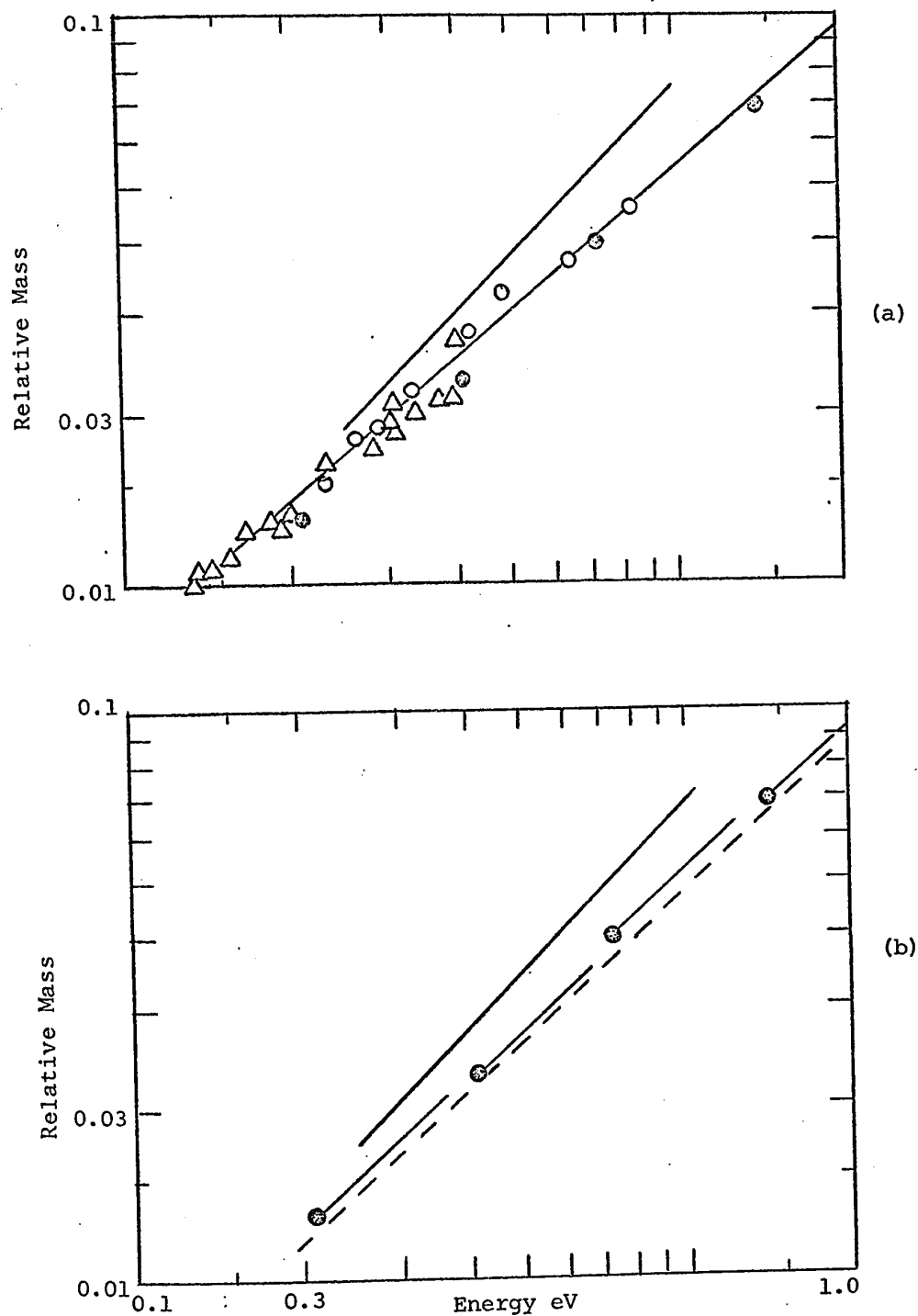


Figure 4.1.2 (a) Effective mass vs. band gap in: $\text{GaIn}_{1-x}\text{Sb}$ (light circles), and InAsSb_{1-x} (triangles) from experimental data of Aubin et al (69A1); dark circles represent GaAs, GaSb, InAs, InSb.

(b) Kane model predicts similar slope: rather less than unity, if the band gap is assumed to vary (with pressure) while E_p and Δ_0 remain constant.

and pressures:

$$m_0^*(T,P) = 0.043 \{E_G^*(T,P)/0.825\}^{0.83} \quad 4.1.15$$

The factor 0.825 is the band gap in GaSb at 0°K (69C4).

The pressure dependence of m_0^* can also be deduced from eq. 4.1.4, in terms of assumed pressure dependences of E_G^* (Table 4.1.A) E_p and Δ_0 . E_p varies so little from one compound to another that its pressure dependence should be insignificant. Δ_0 does vary from one compound to another (69C1), and with alloying (72B2), but Kosicki (see Paul, 66P1) has found that Δ_0 in GaSb is independent of pressure. As shown in Fig. 4.1.2(b), the variations of m_0^* with E_G^* in four III-V compounds, deduced from eq. 4.1.4 assuming E_p and Δ_0 independent of pressure, fit a slope of 0.87, which is close enough to 0.83 for present purposes. De Meis (see Paul, 66P1) has measured the pressure dependence of m_0^* in GaAs (using Faraday rotation) and has shown the results to be consistent with theoretical arguments similar to the above.

The Density of Electrons

The density of electrons in a spherically-symmetric band is:

$$n = \frac{1}{\pi^2} \int_0^\infty f(E) k^2(E) \frac{dk}{dE} dE \quad 4.1.16$$

where $f(E)$ is the Fermi-Dirac function. If the band is also parabolic, with effective mass m^* and $E \propto k^2$,

$$n = \frac{1}{2\pi^2} \left(\frac{2m^*k_B T}{\hbar^2} \right)^{3/2} F_{1/2}(\eta) \quad 4.1.17$$

where η is the reduced Fermi energy E_F/kT , and

$$F_\nu(\eta) = \int_0^\infty \frac{x^\nu}{1+e^{x-\eta}} dx \quad 4.1.18$$

defines the general Fermi integral. The modified form

$$F_\nu(\eta) = F_\nu(\eta)/\Gamma(\nu+1) \quad 4.1.19$$

(See 55D1) has many practical advantages, one of which - existence for negative integral values of ν - is used in equ. 4.2.17.

For a band having ellipsoidal energy surfaces, which in practice goes with the existence of multiple valleys, the density of states per valley is given by eq. 4.1.17 with m^* defined as a mean of the longitudinal and transverse masses:

$$m^* = (m_l m_t^2)^{1/3} \quad 4.1.20$$

In the fully-degenerate limit for a spherically-symmetric band,

$$n = k_F^3/3\pi^2 \quad 4.1.21$$

where k_F is the radius in k -space of the Fermi surface within the band. For ellipsoidal energy surfaces this equation requires the inclusion of a constant factor: the ellipticity $K = m_l/m_t$. Then k_F represents

the value of k at E_F along any transverse direction.

For a spherically-symmetric but non-parabolic band under general statistics, k and kdk/dE may be obtained from eqs. 4.1.6 and 4.1.7.

Van Tongerloo (69T1) gave the resulting electron density as

$$n = \frac{1}{2\pi^2} \left(\frac{2m_o^* k_B T}{h^2} \right)^{3/2} [F_{1/2}(\eta) + \left(\frac{5}{2} - 5\gamma \right) \beta F_{3/2}(\eta) + \left(\frac{7}{8} - \frac{21}{2} \gamma \right) \beta^2 F_{5/2}(\eta) - \left(\frac{1}{4} + \frac{7}{2} \gamma \right) \beta^3 F_{7/2}(\eta)] \quad 4.1.22$$

where $\gamma = m_o^*/m$ and $\beta = k_B T/E_G$. He also found this relation to be good up to $E \sim 1\text{eV}$ in both GaAs and InSb.

4.2 ELECTRON SCATTERING

Scope

This study is more detailed than that needed for determination of only the $\langle 000 \rangle$ to $\langle 111 \rangle$ band separation in GaSb-rich alloys, and was pursued with the object of replacing certain adjustable parameters defining the pressure variation of mobility by a built-in pressure dependence arising naturally from the theory. It was hoped to determine in this way the value of the interband scattering coefficient and perhaps to explain the unexpectedly large variation of apparent mobility with pressure in some alloy specimens.

The work of Basinski (72B1) prior to and during this study was extended by considering in more detail the roles of light and heavy electrons in charged-centre scattering, and by considering alloy scattering and electron-electron scattering.

Brooks' expression for alloy scattering was modified to allow for non-parabolic bands, and for non-linearity (bowing) in the variation of band-gap with composition. Various objections to the formula will be discussed.

Theoretical studies by McLean and Paige (65M1) and others have clearly shown the importance of electron-electron (e-e) scattering when charged-centre (cc) scattering is the dominant "true" (momentum-dispersive) scattering mechanism. Variational calculations of this type seemed too cumbersome to apply to the present miscellany of specimens, but within

the restrictions of the relaxation time approximation the e-e scattering was considered in its proper context, that is, in its effect on the relaxation-time/energy distribution $\tau(E)$ due to all the true scattering mechanisms combined.

General Review

In semiconductors the carriers are confined to regions of the Brillouin zone surrounding the band extrema, (valleys) so that scattering events are sharply divided between those of small changes Δk in the wave-vector: intravalley scattering, and those of large Δk : intervalley scattering and interband scattering between equivalent and non-equivalent valleys respectively. Different scattering mechanisms and theory apply to these divisions. Elastic scattering, where the carriers remain within a given energy range during many collisions, has been assumed in the following pages, yielding an energy-dependent relaxation time $\tau(E)$, with the mobility found by averaging.

We are especially concerned with scattering in the $\langle 000 \rangle$ band, since this is highly pressure-dependent. In this band, the important scattering mechanisms include polar-optical, charged-centre, and perhaps alloy scattering. Interband scattering becomes important when other bands become populated. Scattering by dislocations, inhomogeneities, and the space charge due to clustered impurities had to be neglected due to lack of information, although their effects may be similar to those of alloy scattering, (62W2). As in the case of unalloyed III-V

compounds, it should be valid to neglect: the non-polar part of the deformation due to optical phonons, all scattering due to the transverse optical phonons, and both polar (piezo-electric) and non-polar scattering by longitudinal and transverse acoustic phonons, (57E1).

Intervalley or interband scattering requires a large value of Δk , which in practice can be supplied only by the emission or absorption of a phonon.

Electron-electron (e-e) scattering between carriers in the same band is unlike other scattering mechanisms since this process conserves energy and momentum within the band. Its effect therefore arises only via its influence on the energy distribution resulting from the true scattering mechanisms, and therefore the effect will be considered after the other scattering effects have been combined.

On the other hand, scattering between electrons or holes in non-equivalent bands (e-e' scattering) must be included with other charged-centre scattering.

Polar-Optical Scattering

Polar-optical scattering involves the absorption or emission of longitudinal-optical phonons of small wave-vector; these have substantial energies $\hbar\omega_L \sim .03$ eV, so the scattering may not always justify the use of relaxation times. However, Conwell and Vassell (68C2) have

discussed the error caused by assuming the relaxation time in GaAs to be given by

$$\frac{1}{\tau_{po}(E)} = \frac{e^2 (\hbar\omega_l)}{4\pi\hbar^2 \epsilon_0} \left(\frac{1}{\kappa_\infty} - \frac{1}{\kappa_0} \right) (2N_{ql} + 1) \cdot \frac{m^*(E)}{\hbar k(E)}$$

where $\kappa_\infty \epsilon_0$ and $\kappa_0 \epsilon_0$ are the high- and low- frequency dielectric constants, and N_{ql} is the phonon distribution function:

$$N_{ql} = [\exp (\hbar\omega_l/k_B T) - 1]^{-1}$$

(In the form given by 68C2, a factor $m_0^* (d\gamma/dE)/(2m_0^*\gamma)^{1/2}$, where $\gamma = \hbar^2 k^2/2m_0^*$, appears in place of the equivalent factor $m^*(E)/\hbar k(E)$ used above.) This formula overestimates the scattering for electrons having energies less than about $3\hbar\omega_l$.

Charged-Centre Scattering

Charged-centre scattering appears to be dominant, and merits careful attention, in our specimens. Barrie (56B1) has generalized for a non-parabolic band the analyses of Brooks and Herring, and of Dingle (55D1), for scattering by ionized impurities. The result can be written as

$$\frac{1}{\tau_{cc}(E)} = \frac{e^4 Z^2 N_f(x) m^*(E)}{8\pi\kappa^2 \epsilon_0^2 \hbar^3 k(E)^3} \quad 4.2.3$$

where N is the density of ionized impurities each carrying Z charges,
and where

$$f(x) = \ln(1+x) - x/(1+x), \quad 4.2.4$$

$$x = (2ak)^2, \quad 4.2.5$$

$$\frac{1}{a^2} = \frac{e^2}{\kappa \epsilon_0 k_B T} \frac{\partial n}{\partial \eta}. \quad 4.2.6$$

The screening radius " a " is the parameter of the screened-Coulomb potential:

$$\phi(r) = \frac{e^2}{4\pi\kappa\epsilon_0} \exp(-a/r) \quad 4.2.7$$

The factor $\partial n / \partial \eta$ reduces to $\frac{1}{2} n F_{-1/2}(\eta) / F_{1/2}(\eta)$ for a parabolic band and in the non-degenerate case it reduces to n for any spherically-symmetric band. In our case we need to express $\partial n / \partial \eta$ more generally, as the sum of contributions from the $\langle 000 \rangle$ and $\langle 111 \rangle$ bands.

From eqs. 4.1.17 and 4.1.22.

$$\begin{aligned} \frac{\partial n_1}{\partial \eta} = \frac{1}{2\pi^2} \left(\frac{2m^* k_B T}{\hbar^2} \right)^{3/2} & \left[\frac{1}{2} F_{-1/2}(\eta) + \left(\frac{5}{2} - 5\gamma \right) \frac{3\beta}{2} F_{1/2}(\eta) + \left(\frac{7}{8} - \frac{21}{2}\gamma \right) \frac{5\beta^2}{2} F_{3/2}(\eta) \right. \\ & \left. - \left(\frac{1}{4} + \frac{7}{2}\gamma \right) \frac{7\beta^2}{2} F_{5/2}(\eta) \right] \end{aligned} \quad 4.2.8$$

$$\frac{\partial n_2}{\partial \eta} = \frac{1}{2\pi^2} \left(\frac{2m^* k_B T}{\hbar^2} \right)^{3/2} 2F_{-1/2}(\eta - \Delta E_{02}/k_B T) \quad 4.2.9$$

In the fully-degenerate limit $\partial n / \partial \eta$ can be found from eq. 4.1.21 by writing (for a single band)

$$\frac{1}{k_B T} \frac{\partial n}{\partial \eta} = \left(\frac{\partial n}{\partial k} \right)_F \cdot \left(\frac{\partial k}{\partial E} \right)_F = \frac{k_E^2}{\pi^2} \cdot \frac{m_E^*}{\hbar^2 k_F} \quad 4.2.10$$

where k_F , m_F^* are to be evaluated at the fermi energy. For the <000> and <111> bands both degenerate, as in heavily-doped GaSb at low temperature and/or high pressure, the result is (see also 65R2)

$$\frac{1}{a^2} = \frac{3\pi^{1/3} e^2}{\hbar^2 \kappa \epsilon_0} (m_{00}^* n_0^{1/3} + m_{22}^* n_2^{1/3}) \quad 4.2.11$$

The interesting point here is that heavy electrons provide more effective screening than light electrons, because a small change in fermi potential causes a larger response (screening) in the band with larger density of states. This difference disappears with vanishing degeneracy and is of little importance at and above room temperature.

Eqs. 4.2.3 to 4.2.9 allow for non-parabolic band shape and general statistics, but the following additional factors should be considered in order to account for all the charged-centre scattering.

1) Both donors and acceptors may be present, the scattering being additive since the sign of the charge is immaterial. Baxter et al (67B1) found evidence that the acceptors commonly occurring in GaSb are doubly-charged, whereas the added donors such as Te should be singly-charged; in adding the effects, acceptors then carry four times the weight.

When there are electrons (or holes) in other bands, they will act as scattering centres, but with the following additional complications:

2) The mass of the carrier (in the present case this is a $\langle 000 \rangle$ electron) may not be negligible compared to that of the scattering centre. Morin and Maita (54M1) have referred to this in calculating the resistivity of intrinsic Ge; in the present case the mass ratios range from about 5:1 upwards, so the $\langle 111 \rangle$ electrons can be considered "heavy" to fair approximation.

3) Since the mobile charged-centres are in rapid motion the dielectric constant which applies is κ_{∞} rather than κ_0 , (71Z1), but if this distinction is made one may ask if κ_0 is entirely correct even for ionized impurities, since the scattered carriers are always in rapid motion. Now the screening potential is only roughly given by eq. 4.2.7; in reality there will be interference effects, giving rise to "haloes" of charge, (see Ziman 64Z1, p. 138), and due to this and other complications the 15% or so difference between κ_0 and κ_{∞} is minor.

4) Since the mobile scattering centres have a net drift velocity of their own in an applied field, there will be a drag effect which will reduce the effectiveness of the scattering when the centres and carriers have the same sign, but will increase the effectiveness when they have opposite signs. McLean and Paige (60M1) obtained numerical solutions of the Boltzmann transport equation, in which the drag effect and the e-e scattering effect were included. The most striking example was the mobility of minority holes in InSb at reduced temperatures, where the drag effect is predominant and the resultant hole drift is in the same direction as

the electron drift, corresponding to a negative mobility as usually defined. The drag effect will also be neglected here.

In addition to these complications, it might seem that mobile scattering centres will be less effectively screened, due to a time-lag in the arrival of screening charges. This is not so, because an electron moves preferentially towards electron-depleted regions which (statistically) form the screen. More precisely, one may consider a coordinate system in which the scattering centre is stationary, in thermal equilibrium with the screening charges.

To summarize the conclusions drawn from points (2), (3) and (4), the $\langle 111 \rangle$ electrons behave approximately as immobile scattering centres. Therefore, the total effective density of charged centres, used in computing the $\langle 000 \rangle$ band mobility, was taken as

$$N_I = N_D^+ + 4 N_A^{--} + n_2 \quad 4.2.12$$

where n_2 is the electron density in the $\langle 111 \rangle$ band.

Moore (67M1) has evaluated three corrections to the Brooks-Herring formula: a correction obtained from higher Born approximations, a multiple-scattering correction to allow for the random occurrence of closely-spaced pairs of impurity centres, and a dressing correction due to the perturbing effect of the impurity centre on the electron wave functions. These corrections reduce the mobility in heavily doped GaAs to about 2/3 of that estimated by Ehrenreich (63E1), and give improved agreement with experiment. Unfortunately, the assumptions used in this analysis are somewhat conflicting, and one of them (the assumption of no

compensation) is invalid in the present case. For these reasons, the corrections have been excluded.

Interband Scattering

Now we turn to interband scattering, considering especially the scattering of $\langle 000 \rangle$ carriers into the $\langle 111 \rangle$ band. This is far more important in determining the $\langle 000 \rangle$ band mobility than is the reverse scattering (which must occur in the steady state) in determining the $\langle 111 \rangle$ band mobility, because the density of states is so much higher in the four equivalent $\langle 111 \rangle$ valleys. Interband scattering into a $\langle 111 \rangle$ valley requires a large transfer of momentum $\hbar \Delta k$ of closely-specified magnitude, directed along a $\langle 111 \rangle$ axis. In the case of GaAs, Conwell & Vassell (68C2) singled out the longitudinal-optical phonons close to the zone boundary in the $\langle 100 \rangle$ direction, as responsible either in emission or absorption for interband scattering of hot electrons. Nathan et al (61N1) discussed the evidence for $\langle 111 \rangle$ to $\langle 100 \rangle$ scattering in Ge at high pressures, based on resistivity measurements by Bridgman (52B1) and their own resistivity and Hall data. Fletcher and Pitt (71F1) extended the Hall measurements to 65Kb, obtaining a more quantitative result for the magnitude of the scattering. In both these papers the phonon energy was neglected. Conwell & Vassell did include this in their analysis, giving the relaxation time as

$$\frac{1}{\tau_B(E)} = \frac{D_{12}^2 v (m^*)^{3/2}}{\pi \sqrt{2} \hbar^2 \rho (\hbar \omega_{Lo}) (e^x - 1)} \left[(E + \hbar \omega_{Lo} - \Delta E)^{1/2} + e^x (E - \hbar \omega_{Lo} - \Delta E)^{1/2} \right] \quad 4.2.13$$

where D_{12} is a coupling constant, ρ is the (mass) density, $(\hbar\omega_{Lo})$ is the phonon energy, ΔE is the band separation energy, and $x = \hbar\omega_{Lo}/k_B T$. $v(m^*)^{3/2}$ represents the density of states in the recipient band, of multiplicity v . Eq. 4.2.13 is not concerned with $\langle ooo \rangle$ band non-parabolicity, because the k -vector is unimportant relative to the large Δk supplied by the phonon. Due to the flatness of the phonon spectrum, all the phonons which contribute to interband scattering can be assumed to have the same energy. Interband scattering becomes more significant for small ΔE , as in GaSb with increasing pressure; unfortunately this corresponds to inelastic scattering, and eq. 4.2.13 is probably not very accurate just when most needed.

Alloy Scattering

The resistance of metallic alloys has been considered by Mott and Jones (58M1, p. 296). From simple reasoning, the resistance should vary as $x(1-x)$, which is experimentally observed, e.g. in alloys of the noble metals. Levitas (55L1) found some evidence of alloy scattering in p-type Si-Ge alloys at 300°K; the mobility fell sharply with increasing Si content, but an expected rise beyond the halfway-point was not explicitly observed, although it was deduced by an extrapolation process. Ehrenreich (59E1) compared the experimental mobility in $\text{InP}_x\text{As}_{1-x}$ with the mobility to be expected from polar-optical scattering alone, using interpolation to estimate suitable values of m_0^* , κ etc, and adjusting the theory to

impose agreement for InP and InAs. The experimental mobility sagged below the theoretical curve by a few percent, which may possibly be significant. Tietjen and Weisberg (65T1) found that the mobility in good-quality $\text{GaP}_{1-x}\text{As}_x$ was independent of x in the range $0 \leq x \leq 0.3$; beyond this the electrons begin to populate the $\langle 100 \rangle$ band, which complicates matters, but it seemed clear that alloy scattering was insignificant. Coderre & Woolley (68C1) found no indication of alloy scattering in $\text{InAs}_{1-x}\text{Sb}_x$ and $\text{Ga}_{1-x}\text{In}_x\text{Sb}$, but this latter case will be re-examined here, since the direct measurement of room-temperature mobilities was not possible at that time, but was achieved in the present work due to the discovery of resistance barriers and means for avoiding them.

Brooks has proposed, in an unpublished suggestion referred to in (55L1) and in (65T1), that in a random solid solution the statistical fluctuation in composition produces a hill-and-valley structure in the band edges which can be treated theoretically like the lattice deformations in thermal scattering. Since the alloy fluctuation is not temperature-dependent, a factor $k_B T$ should be omitted in the analysis, and in place of the deformation potential should appear $|E_1 - E_2|$ the difference in band gaps for the unalloyed semiconductors. This proposal involves a theoretical concept: that of representing the aperiodic part of the crystal potential by a point-to-point fluctuation in band gap. This is certainly valid so far as the longer-wavelength Fourier components of the aperiodic potential are concerned, but the concept of band gap becomes obscure with respect to short-wavelength components. From the theory of amorphous

materials having only short-range order (65G1), the band gap should be blurred rather than undulating. Consideration of the Rayleigh-Jeans formula for optical scattering indicates that this difficulty may be unimportant in actuality: scattering varies as λ^{-4} , where λ is the optical wavelength. Long-wavelength radiation is thus only weakly scattered, and by inverting the argument one can see that for a given optical wavelength the scattering is caused preferentially by the longer-wave Fourier components of an aperiodic (scattering) medium.

Apart from the above difficulty, the Brooks proposal seems questionable on the grounds that the hill-and-valley structure would be concentrated in the minority-carrier band, the majority-carrier band being smoothed out due to equalization of the Fermi level if the ionized impurity concentration does not fluctuate, and if it does fluctuate this brings in a new variable not uniquely tied to composition. (Note that this objection does not apply to thermal deformation scattering, which allows implicitly for fluctuations away from the time-average which the Fermi level represents.)

According to (65T1) the Brooks formula can be written as

$$\mu_A = \frac{(2\pi)^{1/2} e \hbar^4 N_a}{3 (k_B T)^{1/2} (m^*)^{5/2} (E_1 - E_2)^2 \times (1-x)} \quad 4.2.14$$

where N_a is the density of lattice sites. This use of N_a need not imply that the important fluctuations are on an atomic scale; it is merely a factor which affects the amplitude of fluctuations of all

wavelengths. Obviously, the larger the value of N_a , the "smoother" is the alloy. If the long-wave fluctuations are the important ones, since these are for statistical reasons of smaller amplitude, the use of $(E_1 - E_2)$ becomes inappropriate when the band gap varies non-linearly with composition. Instead we should use at least the first term $(\frac{\partial E_G}{\partial x})$ of a Taylor expansion about the mean band gap. This would imply that the alloy scattering should become very small near a band gap minimum. To justify the neglect of higher terms, we may consider the "important" electrons of energy $2k_B T$ to $3k_B T$ in GaSb-rich alloys. Fig. 4.1.1 indicates these to have wave-vectors of about $1/40$ of one zone period $2\pi/a_0$, corresponding to a quarter-wavelength of $10 a_0$. A small volume of dimensions $10a_0$ contains 4000 atoms on each sublattice, and from simple statistics (see e.g. 60R1 p. 28) the random fluctuations in alloy composition within this volume should be of order $(4000)^{1/2}/4000$ or less than 0.02. Fluctuations of this small magnitude would have no importance in the region of the band-gap minimum, indicating that alloy scattering should indeed fall to a low value.

For our purposes, we also wish to express the alloy scattering as a relaxation time, in a form which is valid for non-parabolic bands. By analogy with thermal lattice scattering as for example the formula given by Zawadski et al (71Z1), we can deduce that

$$\frac{1}{\tau_A(E)} = \frac{x(1-x) \left(\frac{\partial E_G}{\partial x}\right)^2 a_0^3 k(E) m^*(E)}{2(\pi/2)^{1/2} \hbar^3} \quad 4.2.15$$

Compared to eq. 4.2.14, N_a has been replaced by $4/a_0^3$, where a_0 is the lattice constant; (only four of the eight atoms per unit cell belong to the sublattice involved in alloying). This is the expression which was actually used in attempting to fit the pressure data. It must be admitted that neither this formula nor any known scattering mechanism explains the rapid variation of apparent mobility with pressure which was actually observed in compositions close to the centre of the alloy range.

Combination of Relaxation Times

It is generally accepted that the resultant relaxation time in a band due to a set of independent scattering mechanisms is given by

$$\tau(E) = 1/\sum_j (1/\tau_j) \quad 4.2.16$$

The mobility can then be calculated by proper averaging of $\tau(E)$ over energy, as detailed in section 4.4. This procedure is more general than that of combining the mobilities obtained by averaging each τ_j separately, which has often been done since the integrals may then be analytically tractable. Except for the interband scattering time, each of the τ_j can be expressed in the form

$$\tau_j(k) \propto k^{-2s}/m^*(k) \quad 4.2.17$$

For example, charged-centre scattering provides $s = -3/2$, as is well known in the parabolic case, when $\tau_j \propto E^{-s}$. In a combination of

scattering with both positive and negative values of s , the resultant $\tau(k)$ variation tends to be less extreme. It is this resultant $\tau(E)$ variation which should be considered when allowing for the effects of e-e scattering between carriers in the same band.

Electron-Electron Scattering

Bate et al (65B1) based their practical approach to this problem on treatments by Appel (61A1), who obtained numerical solutions of the Boltzmann transport equation by the variational technique, and by Keyes (58K1), whose less exact treatment involved tedious integrals. Bate et al found that in the artificial case when e-e collisions were far more frequent than e-donor collisions, Keyes' result could be expressed in terms of standard integrals. The mobility due to a scattering mechanism characterized by the usual law (for a parabolic band) $\tau \propto E^{-s}$, would be reduced, due to "strong" e-e scattering by a factor

$$\phi_{ee} = \frac{\mu_{ee}}{\mu_o} = \frac{[3/2 F_{1/2}(n) \Gamma(3/2)]^2}{(3/2 + s)(3/2 - s) F_{1/2+s}(n) F_{1/2-s}(n) \Gamma(3/2+s) \Gamma(3/2-s)}$$

4.2.17

Fig. 4.2.1 shows the form of $\phi_{ee}(n, s)$ for $s = \pm 3/2$, ± 1 and $\pm 1/2$.

For $s = 0$ the mobility would be unaffected by e-e collisions.

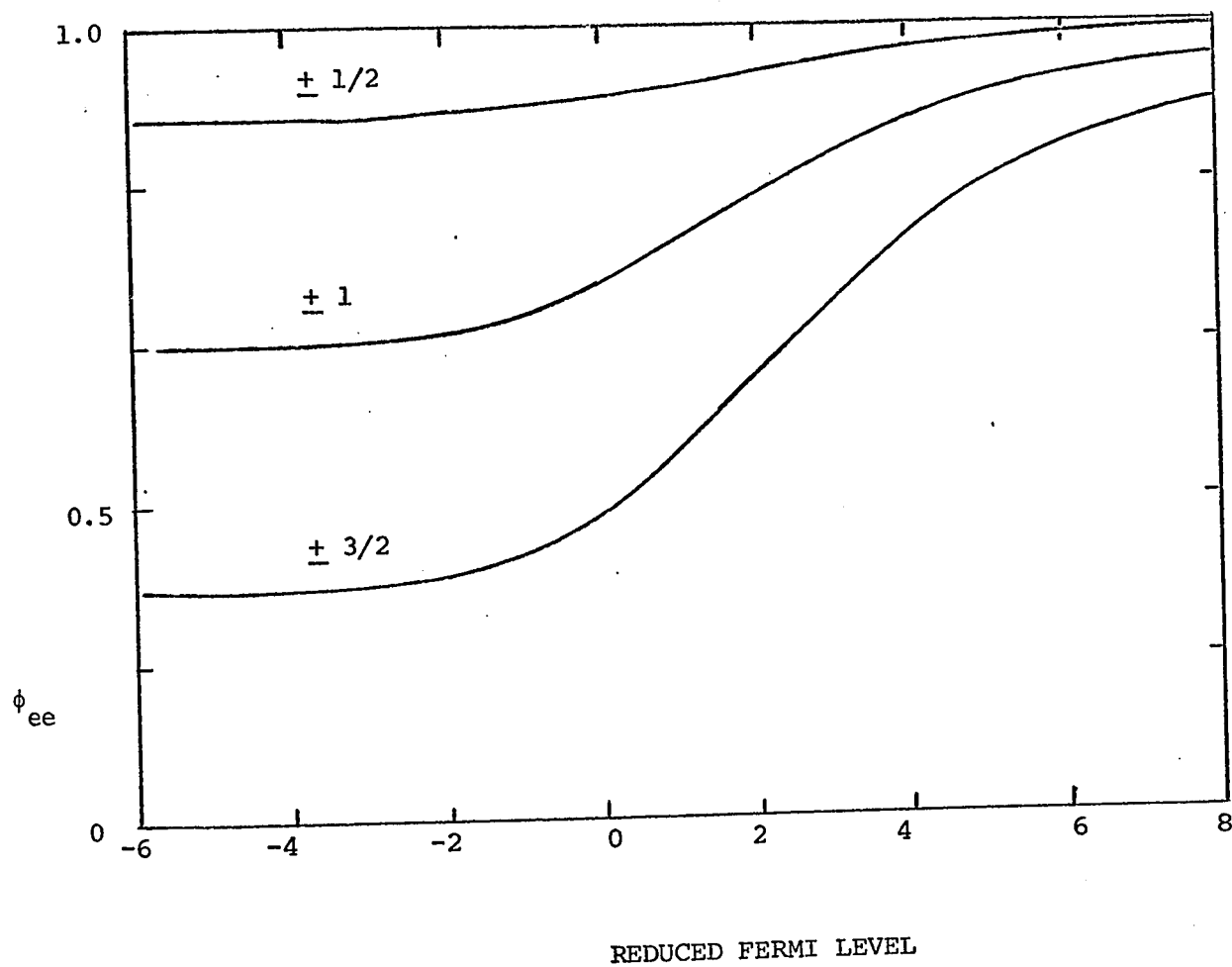


Figure 4.2.1. Mobility reduction due to "strong" electron-electron scattering, for various values of s , where $T \propto E^{-s}$

For non-degenerate, ionized-impurity scattering, (i.e. $\eta < 1$, $s = -3/2$) it can be seen that $\phi_{ee} = 0.294$. The factor obtained by Appel for the usual case, when e-e collisions and e-donor collisions have equal frequency, was 0.573, which is almost midway between ϕ_{ee} and unity. Bate et al then proposed a weighting factor $\alpha \approx 1$ and assumed this to remain unchanged with increasing degeneracy where variational results were unavailable. They also coupled this proposal with a different approach to the effect of e-e collisions on the polar scattering, to deduce the conductivity at 80°K in InSb by a rather artificial combining of two relaxation times. For present purposes, where interband and alloy scattering have also to be considered, it seemed more natural to allow for the non-charged-centre scattering by choosing a modified value of s . Inspection of the relaxation time/energy relations as evaluated numerically for the present specimens revealed that a value $s = -1$ was much closer than $-3/2$ in all cases. It seemed unnecessary to distinguish closer gradations of s than this, since the $\langle 000 \rangle$ band e-e collisions in GaSb-rich specimens are in any case less significant, due to the larger number of collisions of the $\langle 000 \rangle$ electrons with donors, compensating acceptors, heavy $\langle 111 \rangle$ electrons and phonons.

An estimate of the mobility reduction due to e-e collisions can then be made by a relation of the form

$$\mu_s / \mu_s^0 = \{1 + \alpha \phi_{ee}(\eta, s)\} / (1 + \alpha) \quad 4.2.18$$

As explained in Section 6.2, the effect on unalloyed GaSb is particularly small: less than 3% reduction, due to the preponderance of $\langle 111 \rangle$ electrons and to the degree of compensation.

4.3 CONDUCTIVITY AND HALL COEFFICIENT IN MULTIBAND CASE

With no applied magnetic field, the conductivity is just the sum of contributions from individual bands:

$$\sigma = e \sum_i n_i \mu_i \quad 4.3.1$$

The expressions giving the carrier densities n_i were described in section 4.1, and the mobility μ_i for the i th band is obtained by proper averaging of the resultant relaxation time $\tau(E)$ (as given by eq. 4.2.16) over energy. For the present analysis only the spherically-symmetric $\langle 000 \rangle$ band will be treated in this way, and for this case,

$$\mu_1 = e \left\langle \frac{\tau}{m^*} \right\rangle \quad 4.3.2$$

where

$$\langle y \rangle = \int_0^\infty \left(- \frac{\partial f_0}{\partial E} \right) y k^3 dE / \int_0^\infty \left(- \frac{\partial f_0}{\partial E} \right) k^3 dE \quad 4.3.3$$

This form of the averaging function can be derived by replacing the velocity-squared factor in the Boltzmann transport integral defining the current, using eq. 4.1.1 for $m^*(E)$, and is valid for any spherically-symmetrical $k(E)$ relation, (61K1), (71Z1). For the $\langle 111 \rangle$ or $\langle 100 \rangle$ bands it is usual to take m^* outside the integral signs, since these bands are sufficiently parabolic over the energy range which is occupied by electrons that m^* is a constant. On the other hand the multiplicity and ellipticity K should be allowed for. When the conductivity is defined by eq. 4.3.1 these factors are implied within the definition of mobility, arising naturally from the anisotropic effective mass tensor.

The Hall coefficient is not just the sum of individual contributions, since each group of carriers on its own would generate a different Hall potential, and a compromise value results, which cancels the total transverse current, but not the individual contributions to the transverse current. A simplified analysis may be found in various texts, (e.g. Smith, 59S1), p. 104 and 119), and this has been generalized for multiple bands by Coderre and Woolley (69C4) in the form

$$R_H = \frac{-\frac{1}{B} \sum_i D_i}{(\sum_i A_i)^2 + (\sum_i D_i)^2} \quad 4.3.4$$

where B is the magnetic field strength, and

$$A = ne^2 \langle \tau / m^* (1 + \omega^2 \tau^2) \rangle \quad 4.3.5$$

$$D = ne^3 B \langle \tau^2 / m^{*2} (1 + \omega^2 \tau^2) \rangle \quad 4.3.6$$

$$\omega = eB / m^*(E)$$

It is convenient to introduce parameters α , β^2 defined as

$$\alpha = e \langle \tau / m^* (1 + \omega^2 \tau^2) \rangle \quad 4.3.7$$

$$\beta^2 = e^2 \langle \tau^2 / m^{*2} (1 + \omega^2 \tau^2) \rangle \quad 4.3.8$$

A subscript i should be attached to each of the quantities A, D, ω , α , β^2 according to the band it represents. The parameter α can be regarded as the mobility at finite magnetic field strength, and involves the ellipticity in the same way as the parameter μ . The related

parameter β^2 represents a field-dependent mobility squared, which involves the ellipticity in a different way. For present purposes the band involving ellipticity, i.e. the $\langle 111 \rangle$ band, satisfies the weak-field approximation: $\omega^2 \tau^2 \ll 1$, and for this case,

$$\beta_2^2 = \mu_2^2 r_2 F_2 \quad 4.3.9$$

where r_2 is an averaging parameter, defined for weak fields as

$$r = \frac{\langle \tau^2 / m^{*2} \rangle}{\langle \tau / m^* \rangle^2} \quad 4.3.10$$

It is well known that for highly degenerate carriers, or in a weak field with τ/m^* independent of energy, the averaging parameter is unity. At the other extreme it takes the value 1.93 for charged-centre scattering of non-degenerate carriers in a parabolic band at low fields.

The factor F_2 brings in the ellipticity:

$$F = 3K(K + 2)/(2K + 1)^2$$

. This factor is of minor importance, since its value is close to unity (≈ 0.8) for actual values of K (≈ 10).

In the analysis of Section 6, the parameters μ_2 and r_2 were empirical values, chosen for best fit to the experimental results, and the Hall coefficient was given by

$$R_H = -\frac{1}{e} \cdot \frac{n_1 \beta_1^2 + n_2 \mu_2^2 r_2 F_2}{(n_1 \alpha_1 + n_2 \mu_2)^2 + (n_1 \beta_1^2 + n_2 \mu_2^2 r_2 F_2)^2 B^2} \quad 4.3.11$$

where the $\langle ooo \rangle$ parameters $\mu_1, \alpha_1, \beta_1^2$ were obtained by proper averaging in some cases. In other cases an empirical mobility μ_1 was chosen for best fit to the data, and α_1 and β_1^2 were found using the relations

$$\alpha = \mu / (1 + \mu^2 B^2)$$

$$\beta^2 = r\mu^2 / (1 + \mu^2 B^2)$$

These relations follow from replacing the factor $1 + \omega^2 \tau^2$ where this appears by the factor $(1 + \mu^2 B^2)$ outside the integral signs, which is a very good approximation in practice. The averaging parameter r_1 was chosen on the basis of experience gained using the proper averaging procedure; this was sufficient since its value was always between unity and 1.1. (This low value results from the combination of scattering mechanisms with opposite $\tau(E)$ vs. E dependence, coupled with appreciable electron degeneracy.)

5. PRESSURE EXPERIMENTS AND RELATED WORK

5.1 REVIEW OF WORK BY OTHERS

Long (55L2) reported resistivity and Hall data in InSb up to 2Kb, and Keyes (55K1) reported resistivity only in InSb up to 12 Kb. Gratton (see section 5.3) has recently extended the Hall measurements to 12 Kb also, all these results being in mutual agreement. Concerning InAs, Taylor (55T1) presented resistivity and Hall data for temperatures in the range -100°C to $+580^{\circ}\text{C}$, and for pressures up to 2 Kb within a more restricted temperature range. The temperature data is in reasonable agreement with that of Madelung et al. (reviewed in 64M1, p. 121) and the present work, provided one assumes that the curves in (55T1) are incorrectly labelled. The pressure data also agrees with the present results (section 5.2) provided one does not take too precisely the statement that the room temperature Hall coefficient was constant with pressure.

The most significant work for our purpose was that of Sagar et al (60S1), (61S1) on Te-doped GaSb, where isotropic pressure measurements up to about 10Kb played a key role in establishing that two conduction bands were occupied at room temperature and pressure. The identification of the second band as having $\langle 111 \rangle$ symmetry was made by applying uniaxial stress. To observe the effect of the higher-lying $\langle 100 \rangle$ minima requires higher pressures, where the differences in behaviour of Te, Se and S-doped

GaSb also become prominent. In this regard, resistivity measurements to 50 Kb have been reported by Kosicki et al (68K1), with references to earlier work where the measurements were limited to lower pressures by lack of a suitable pressure fluid, capable of transmitting higher pressures isotropically. Using a different type of apparatus, Pitt (69P1) measured resistivity and Hall coefficient in Te-doped GaSb to 65 Kb under an approximation to hydrostatic conditions, which involved cutting the specimens parallel to the $\langle 100 \rangle$ direction. This work confirmed the location of the $\langle 100 \rangle$ minima as about 0.31 eV above the $\langle 000 \rangle$ minimum, and gave information as to the $\langle 100 \rangle$ band mobility, but the specimen had anomalously - low mobility in the central band, and the resistivity increase beyond 25 Kb was greater by an order of magnitude than that reported as characteristic of Te-doped GaSb, (68K1).

Concerning GaAs, perhaps the most recent extensive work has been reported by Pitt and Lees (70P1) using the same apparatus as in (69P1). This paper includes a useful review of the present understanding of GaAs, and confirms that the $\langle 100 \rangle$ minima lie about 0.38 eV above the central minimum.

Very few pressure experiments have been reported on III-V alloys. Craford et al (68C3) reported the pressure-dependence of resistivity at and below room temperature in $\text{GaP}_{1-x}\text{As}_x$ at compositions such that the $\langle 000 \rangle$ and $\langle 100 \rangle$ minima were close in energy at low pressures, and from these and photoconductivity measurements deduced the influence of the relative positions of these minima on the energies of Te and S donor

impurity levels. Similar effects in Te- and Se-doped GaSb have been reported by Kosicki and Paul (66K1), who also discussed the nature of this influence. The pressure dependence of resistance up to 28 Kb in $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ has been reported by Lorenz et al (69L1) for two compositions: $x = 0.3$ and 0.5 ; the band separations obtained from this are in good agreement with those of Coderre and Woolley (69C4), obtained from the temperature variation of resistivity and Hall coefficient. Data on the relative positions of the $\langle 000 \rangle$ and $\langle 100 \rangle$ minima in $\text{Ga}_x\text{In}_{1-x}\text{P}$ has been obtained by Hakki et al (70H1) using the pressure dependence of the forward bias voltage at constant current in pn junctions.

No pressure results have been reported for the $\text{GaAs}_x\text{Sb}_{1-x}$ system, and the only measurements of any kind (apart from metallurgical studies) seem to have been: the optical absorption work of Thomas et al (70T2) which yielded the band gap data used here, several resistivity and Hall runs by Coderre (69C3) on GaAs-rich specimens only, and the mobilities (of holes) reported by Clough & Tietjen (69C2) in the composition range $0.2 \leq x \leq 1.0$; (see section 7 in this regard). Also, Taylor and Fortin (70T1) investigating the spectral response of the photoconductivity at temperatures between 100°K and 300°K , are in agreement with (70T2). Fillion (72F1) has reported on his magneto-optical studies at 4.2°K . These investigations provided no information about the $\langle 000 \rangle$ to $\langle 111 \rangle$ band separation, nor on electron transport except for extreme GaAs-rich specimens.

5.2 PRESSURE MEASUREMENTS ON SPECIMENS CONTAINING GaSb

The pressure results obtained on specimens containing GaSb are the most significant of the present work, and will next be presented. It should be apparent from section 5.1 that no room-temperature electron transport measurements of value, nor pressure results of any kind, have previously been reported for GaSb-rich alloys.

The first pressure measurements were essentially a repeat of these reported by Sagar (60S1) on Te-doped GaSb, and produced equivalent results. Two specimens were used, having Hall coefficients of 31.6 and $8.58 \text{ cm}^3/\text{C}$ at room temperature and pressure. The second of these was cut from the same single-crystal ingot as used by Harland and Woolley (66H1) and by Basinski (72B1).

Eight specimens of $\text{GaAs}_x\text{Sb}_{1-x}$ were measured, covering the range $0. \leq x \leq 0.36$. These were all selected from ingot TZF6. Twelve specimens of $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ were measured, the most useful of these being selected from ingots TZA2 and TZA3.

General data on all these specimens are shown in Table 5.2.A. The pressure results are shown in Figs. 5.2.1 to 5.2.4. (The smooth and dotted curves are theoretical variations, discussed in Section 6.2.) Characteristic features of all these curves, for example the positions of the Hall maxima, show clear dependence on alloy composition, especially when allowances are made for differences in electron concentration, as was done in the analysis.

Table 5.2.A

General data on specimens containing GaSb

LIST #	identification ingot/cm		x	dopant	asym. ratio	ρ_o ohm-cm	R_{HO} cm ³ /C	n_{HO} 10 ¹⁸ cm ⁻³	μ_{HO} cm ² /vs
1	GaSb1	GaSb	/	Te	1.25→1.24	.0088	31.6	0.188	3590.
2	GaSb2		/	Te	1.12→1.14	.00286	8.58	0.73	3000.
3	TZF6/11.7	GaAs _x Sb _{1-x}	.012	Te	8.2 →8.8	.0806	9.86	0.63	122.
4	TZF6/9.8		.024	Te	1.45→1.44	.00316	8.72	0.72	2760.
5	TZF6/8.7		.062	Te	4.0 →3.95	.00223	6.16	1.01	2760.
6	TZF6/8.1		.110	Te	1.30→1.34	.00233	5.09	1.22	2190.
7	TZF6/7.8		.130	Te	2.0 →1.85	.00174	4.20	1.48	2410.
8	TZF6/7.2		.275	Te	2.3 →1.8	.00221	2.62	2.38	1183.
9	TZF6/6.5		.345	Te	5.4 →9.3	.00375	2.34	2.65	625.
10	TZF6/5.1		.36	Te	1.1 →1.2	.00335	2.57	2.43	769.
11	DFA4/3.3	Ga _x In _{1-x} Sb	.96	Te	7.05→7.5	.0103	21.4	0.29	2070.
12	TFA13/1.5		.96	Te	1.47→1.25	.0018	7.43	0.84	4080.
13	TZA3/10.0		.92	Te	1.08→1.11	.00132	7.05	0.89	5360.
14	TZA3/10.4		.89	Te	2.28→2.55	.00101	5.84	1.07	5800.
15	TZA2/2.4		.88	Te	59. →50.	/	39.0	0.16	/
16	TZA3/10.9		.855	Te	1.09→1.15	.00844	4.71	1.32	5580.
17	TZA2/3.9		.81	Te	4.10→3.44	.0058	22.8	0.275	3950.
18	TZA3/11.3		.805	Te	1.1 →1.05	.000482	3.51	1.78	7280.
19	TFA3/4.3		.58	Te	1.10→1.13	.000631	1.87	3.30	2963.
20	TFA8/8.7		.38	/	1.48→1.40	.00230	23.5	0.265	10,240.
21	TFA8/10.6		.21	/	1.07→1.09	.000645	13.4	0.470	20,820.

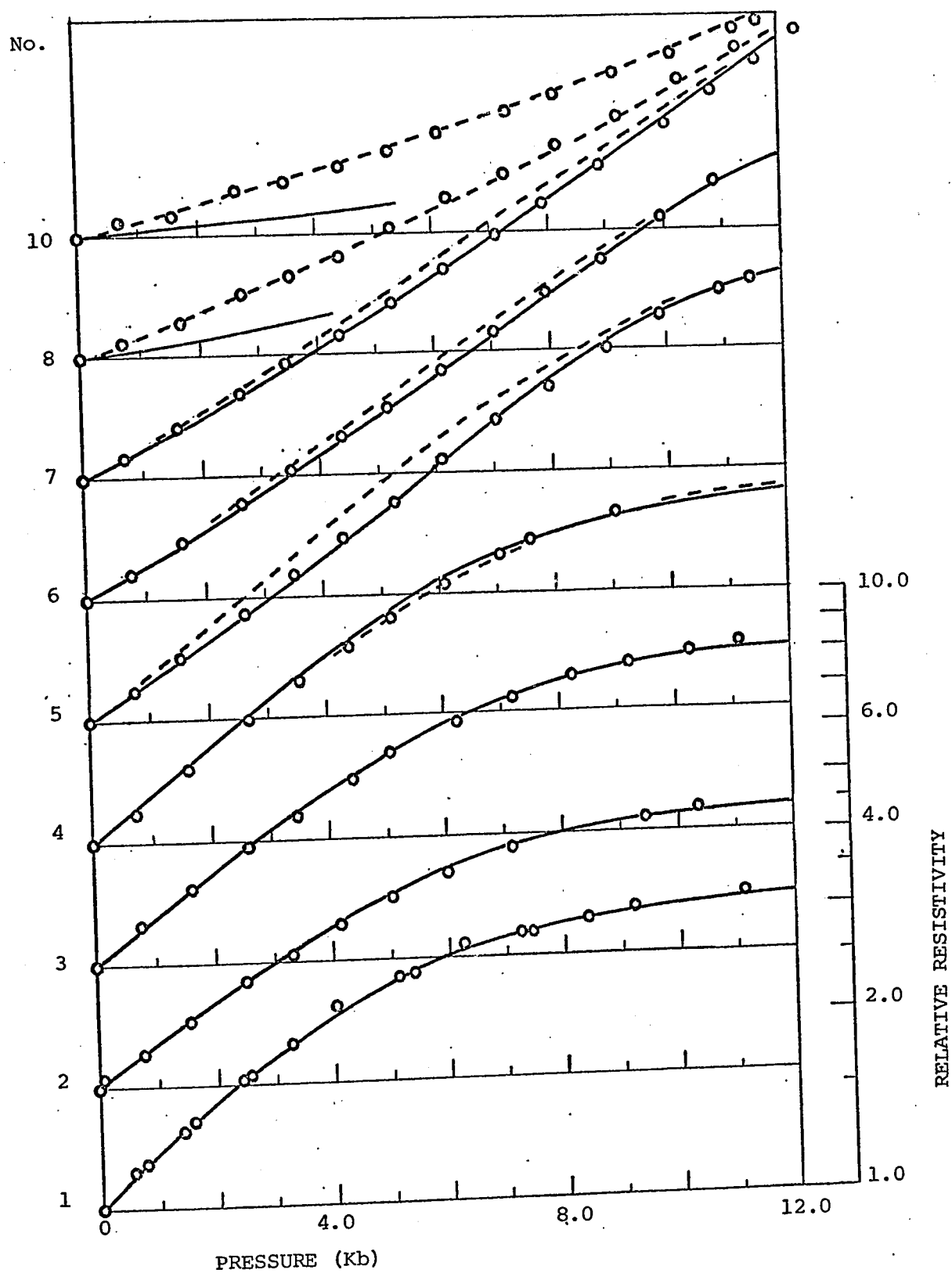


Figure 5.2.1. Experimental pressure dependences of resistivity in GaSb and GaAsSb_{1-x} . The vertical scale is logarithmic, with successive sets of data offset for clarity; the curves are theoretical variations.

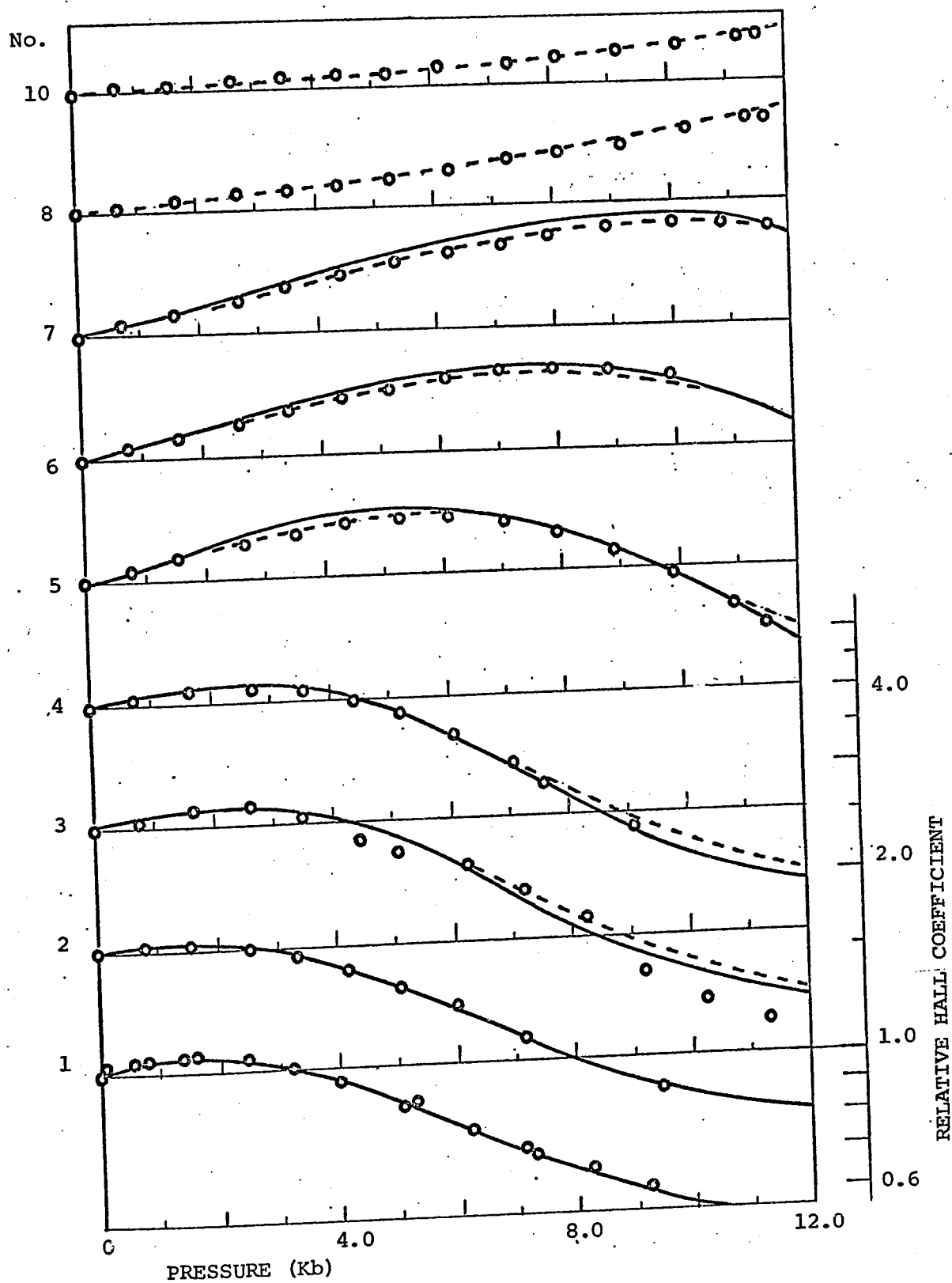


Figure 5.2.2. Experimental pressure dependences of Hall coefficient in GaSb and GaAs_xSb_{1-x}. The vertical scale is logarithmic, with successive sets of data offset for clarity; the curves are theoretical variations.

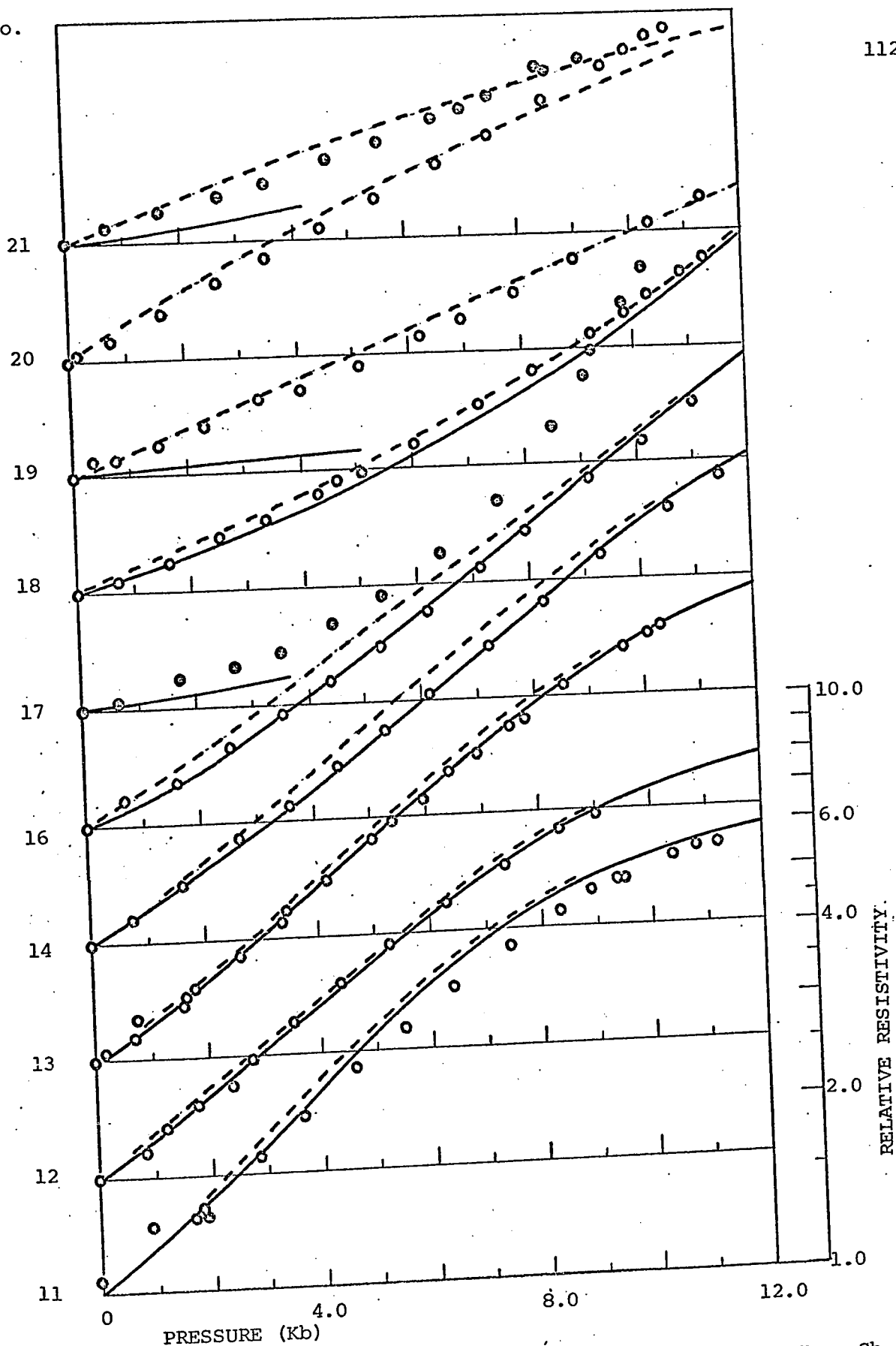


Figure 5.2.3. Experimental pressure dependences of resistivity in $\text{Ga}_x\text{In}_{1-x}\text{Sb}$. The vertical scale is logarithmic, with successive sets of data offset for clarity; the curves are theoretical variations.

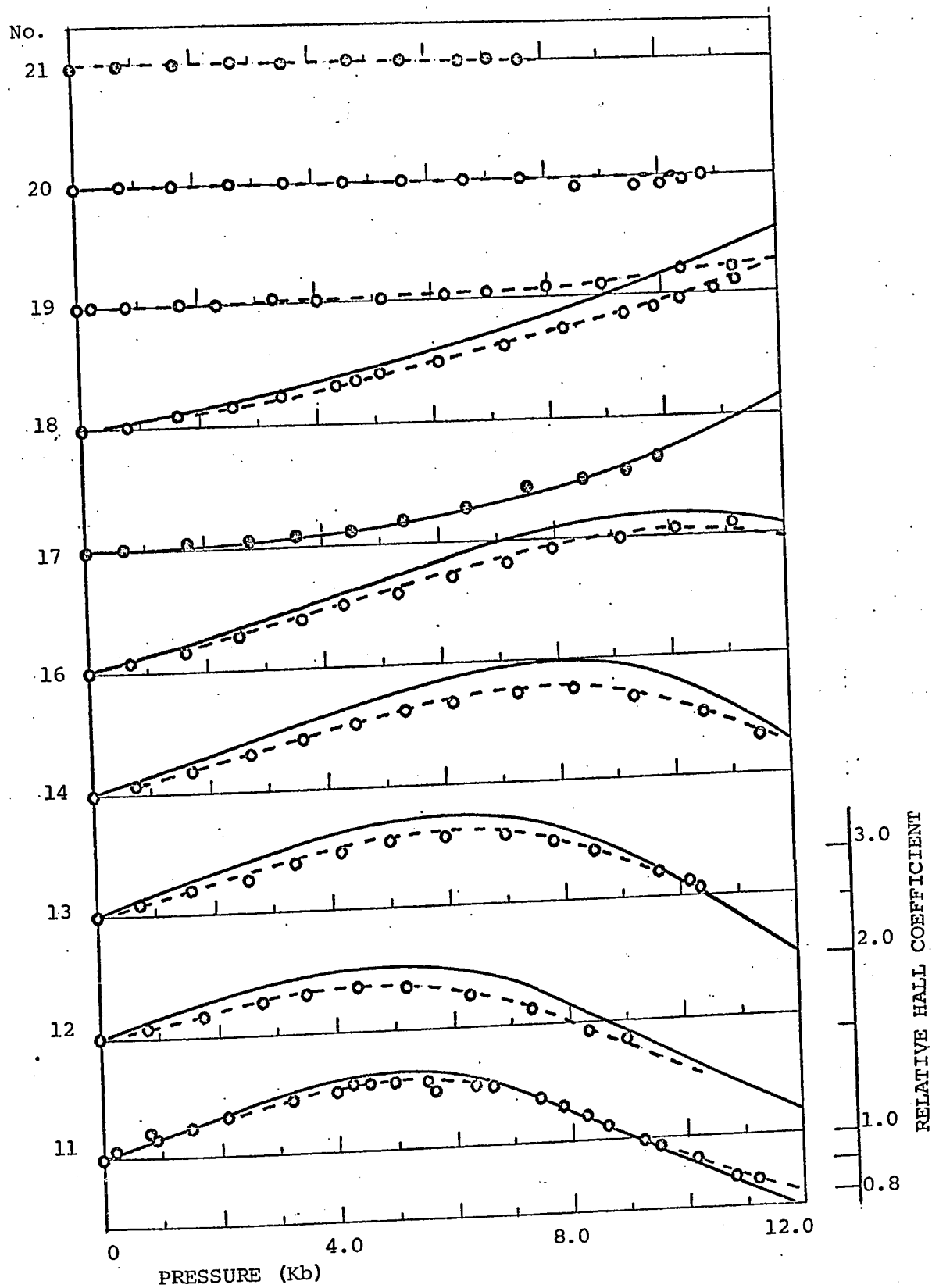


Figure 5.2.4. Experimental pressure dependences of Hall coefficient in $\text{Ga}_x\text{In}_{1-x}\text{Sb}$. The vertical scale is logarithmic, with successive sets of data offset for clarity; the curves are theoretical variations.

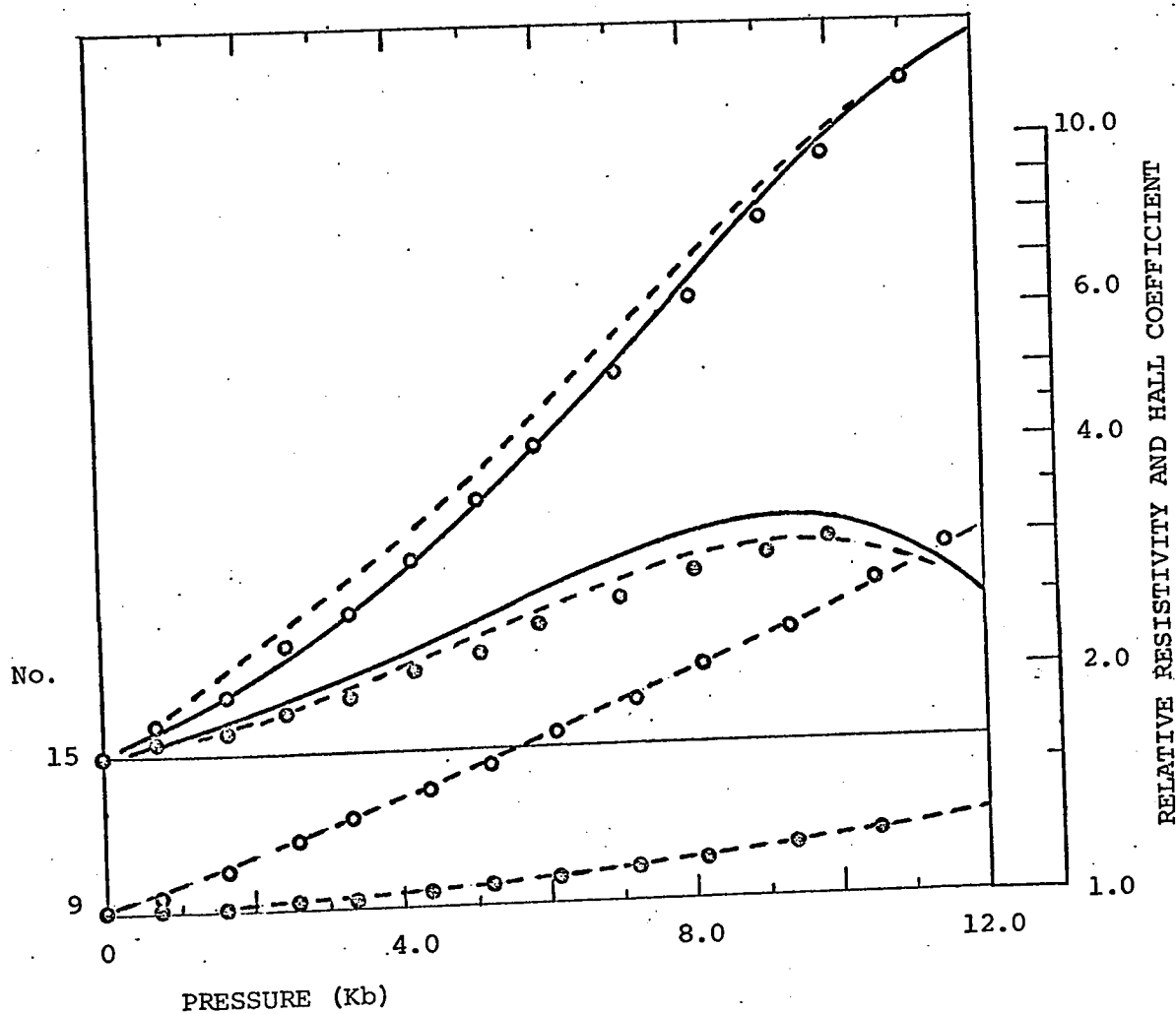


Figure 5.2.5. Experimental pressure dependences for two highly asymmetric specimens: numbers 9 and 15 of Table 5.2.A. Light circles show resistivities, and dark circles the Hall coefficients. The curves are theoretical variations.

Fig. 5.2.5. shows the behaviour of specimens with high, variable asymmetry (due to the presence of resistance barriers), one example being taken from each of the two alloy systems. By their resemblance to the behaviour of specimens chosen to avoid barriers so far as possible, these demonstrate clearly that the barriers need not prevent one from drawing meaningful conclusions from the results. The principal drawback lies in uncertainty as to the absolute mobilities.

These experimental pressure data are uncorrected for dimensional compression, (Section 3.1) which is negligible compared with the other effects in specimens containing GaSb.

5.3 PRESSURE MEASUREMENTS ON SPECIMENS CONTAINING InAs

Specimens containing InAs were measured both for their inherent interest, especially in the case of the $\text{InAs}_x\text{Sb}_{1-x}$ materials prepared during the present project, and also for comparison with the GaSb-family of results.

Three specimens of unalloyed InAs were measured; two of these were undoped commercial material from different sources, having electron densities a little over 10^{16} cm^{-3} as is usual in this material; the third specimen was heavily Se-doped to $6 \times 10^{19} \text{ cm}^{-3}$ apparent electron density, and was taken from the most heavily-doped of a series of ingots prepared by R. Senechal of this department. As discussed in section 6.3, it has been thought that such heavily-doped InAs contains an appreciable fraction of the electrons in higher conduction band

minima near the $\langle 111 \rangle$ or $\langle 000 \rangle$ extremities of the Brillouin zone, and it was therefore of particular interest to examine the pressure dependences of the above specimens.

Only three specimens from the $\text{InAs}_x\text{Sb}_{1-x}$ system were measured; initially this was due to technical difficulties (leaks) when the apparatus was newly-built and unfamiliar; by the time these were solved the task of examining the pressure-dependence of this alloy system was assumed by M. Gratton of this department. He has since made a comprehensive series of pressure measurements on this system, including unalloyed high purity InSb.

The $\text{Ga}_x\text{In}_{1-x}\text{As}$ system was represented by two specimens taken from material prepared by earlier workers in the department.

General data on the specimens measured in the present work are summarized in Table 5.3.A, and the pressure results are shown in Figs. 5.3.1 to 5.3.3., uncorrected for dimensional compression.

The pressure-increase in Hall coefficient in the undoped InAs specimens indicated an unexpected freezing out of about 0.2×10^{16} electrons cm^{-3} in both cases; since an intrinsic contribution was not expected at electron densities above 10^{16} cm^{-3} , (as was verified by calculations allowing for degeneracy and non-parabolicity), the resistivity and Hall coefficients of the Monsanto specimen were measured as a function of temperature (at atmospheric pressure) between -80°C and $+200^\circ\text{C}$. The results correlated closely with those of Madelung et al (64M1, p. 121, curve B) on a similar specimen. It was also established that the Hall coefficient of the Monsanto specimen remained independent of magnetic field strength within 0.1% up to at least 20 K Gauss at room temperature.

TABLE 5.3.A.

General data on specimens containing InAs

list #	identifi- cation ingot/cm	x	do- pant	asymmetry ratio	ρ_o	R_{Ho}	n_{Ho} 10^{18} cm^{-3}	μ_{Ho} cm^2/Vs
22	Monsanto*	/	/	1.09+1.09	.0194	429.0	.0156	22,140.
23	Cominco	/	/	1.3 +1.35	.00685	168.0	.037	24,560.
24	RSUO. #	/	Se	1.56+1.62	8.9×10^{-5}	0.10	62.0	1,135.
25	$\text{InAs}_{1-x}\text{Sb}_x$ TZC11/7.4	.62	/	1.58+1.50	.00406	87.8	.071	21,700.
26	$\text{InAs}_{1-x}\text{Sb}_x$ TZC10/7.5	.72 [†]	/	1.54+1.66	.00293	77.7	.080	26,500.
27	$\text{InAs}_{1-x}\text{Sb}_x$ TZC10/0.8	.84	/	1.40+1.38	.00557	151.0	.0415	27,200.
28	$\text{Ga}_{1-x}\text{In}_x\text{As}$ TFB1/10.5	.1	not known	1.06+1.04	.000336	2.71	2.3	8,050.
29	$\text{Ga}_{1-x}\text{In}_x\text{As}$ TFB3/1.8	.46	/	1.00+1.08	.013	107.	.058	8,250.

* highest purity, single crystal + not homogeneous by X-ray

heavily doped, prepared by R. Senechal of University of Ottawa

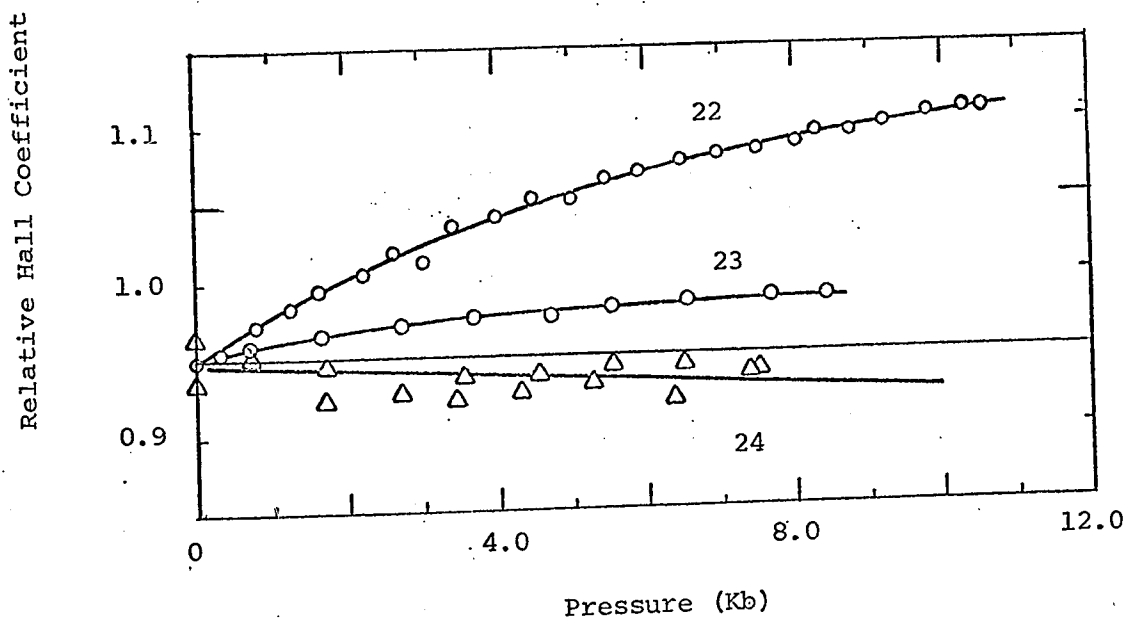
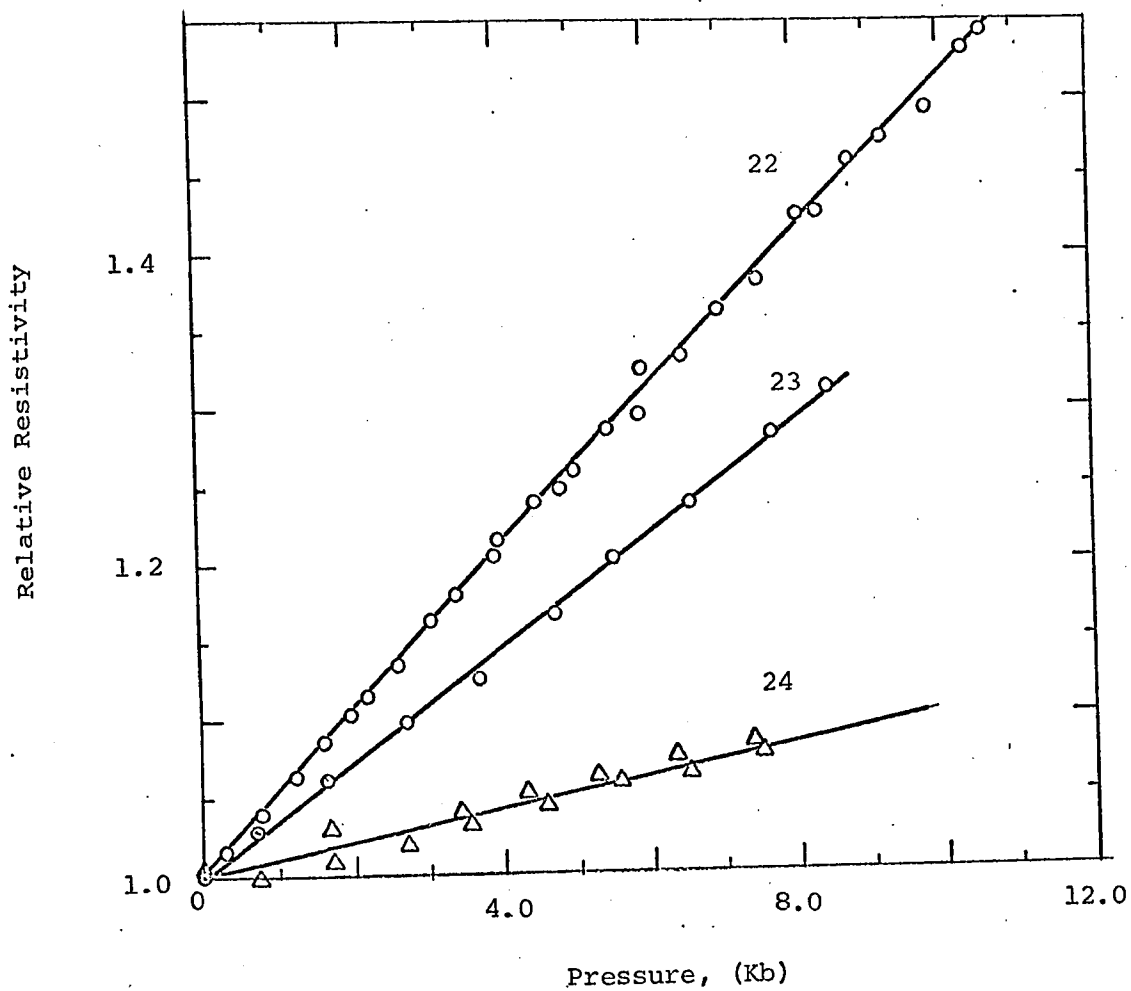


Figure 5.3.1 Experimental pressure dependences in undoped (22, 23) and in heavily Se-doped (24) InAs specimens.

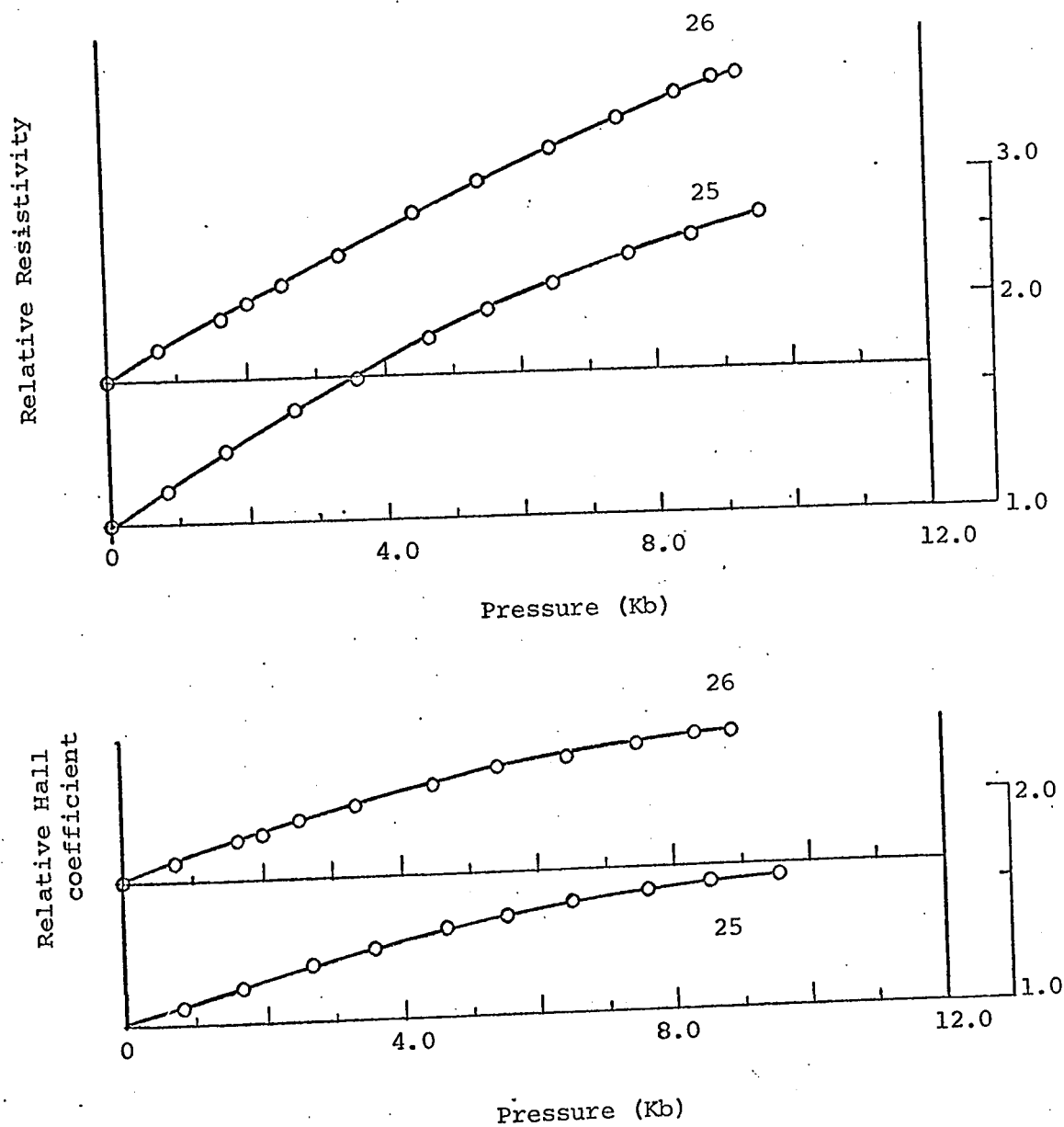
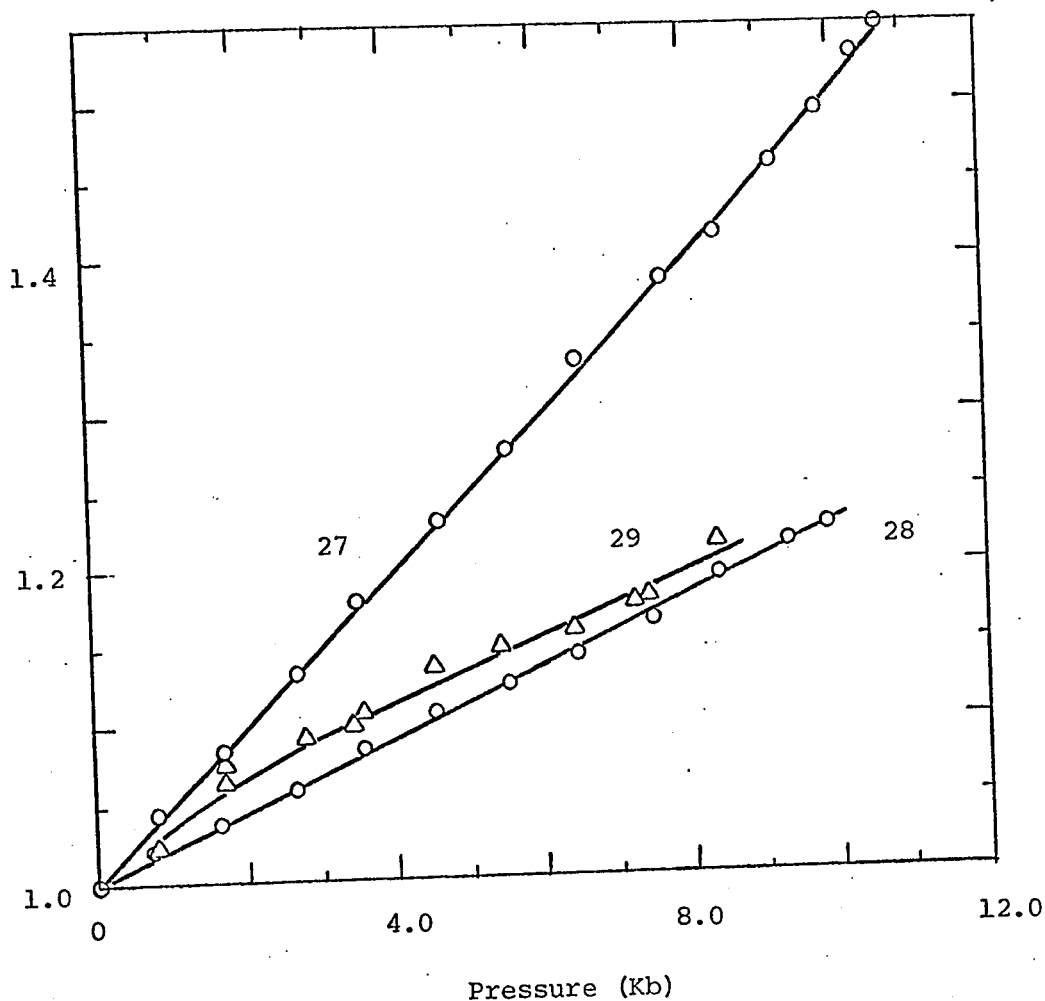


Figure 5.3.2 Experimental pressure dependences in InAsSb_{1-x} .
 The vertical scales are logarithmic, with curves
 offset for clarity.

Relative Resistivity



Relative Hall coefficient

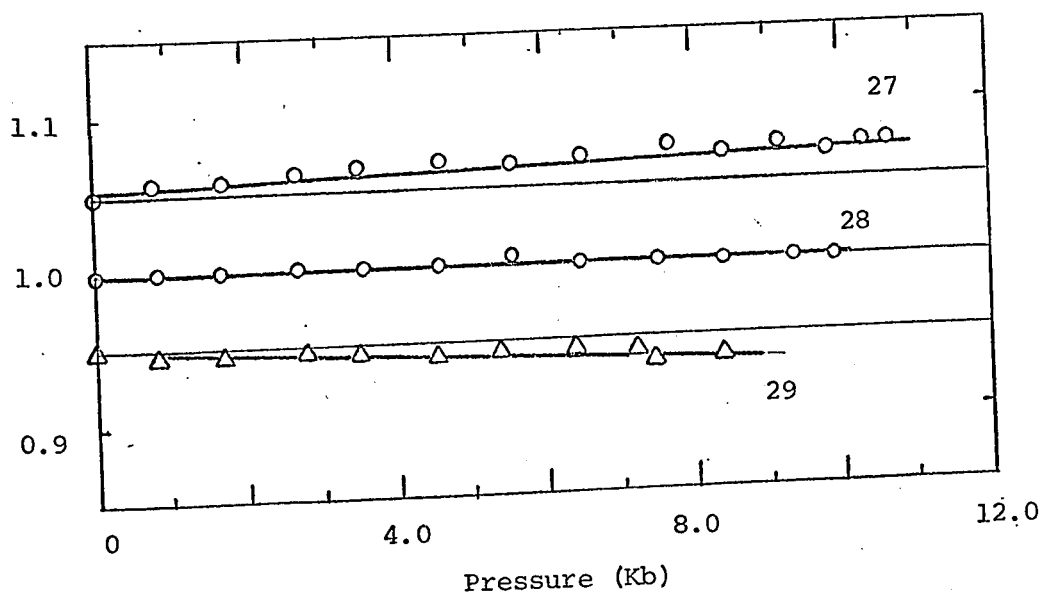


Figure 5.3.3. Experimental pressure dependences in $\text{InAs}_{1-x}\text{Sb}_x$ (specimen 27) and $\text{Ga}_{1-x}\text{In}_x\text{As}$ (specimens 28, 29)

6. ANALYSIS

6.1 APPLICATION OF THE THEORY

Preliminary approximations

For preliminary analysis of two-band transport we may regard the effect of both pressure and composition changes as varying the band separation ΔE , but no other structural parameter. We may also assume parabolic bands, non-degenerate statistics, and constant mobility in each band, with averaging parameters equal to unity. The total electron density will be independent of pressure if there is no freeze-out to impurity levels. If we then apply increasing pressure to a specimen having all the electrons initially in the central band, there will be a regime of two-band conduction over a certain pressure range, where equations 4.3.1 and 4.3.8 reduce to:

$$\sigma = e(\mu_1 n_1 + \mu_2 n_2) = e\mu_2 N[b(1+v) + v] \quad 6.1.1$$

$$R_H = \frac{(\mu_1^2 n_1 + \mu_2^2 n_2)}{e(\mu_1 n_1 + \mu_2 n_2)^2} = \frac{1}{eN} \frac{b^2(1-v) + v}{[b(1-v) + v]^2} \quad 6.1.2$$

where $N = n_1 + n_2$, $v = n_2/N$, $b = \mu_1/\mu_2$. R_H then reaches a maximum value given by

$$R_H/R_{Ho} = (b + 1)^2/4b \quad 6.1.3$$

at the pressure for which

$$v/(1-v) = b \quad 6.1.4$$

At this point the two bands contribute equally to the conductivity, which is given by

$$\sigma/\sigma_o = 2/(b + 1) \quad 6.1.5$$

To express R_H in terms of ΔE , let $\Delta = \Delta E/k_B T$, writing Δ_m for the value of Δ which yields the maximum in R_H , and let c be the ratio of the density of states in band 2 to that in band 1.

Then eq. 6.1.4 is equivalent to

$$ce^{-\Delta_m} = b \quad 6.1.6$$

and R_H can be expressed as

$$R_H/R_{Ho} = \frac{(b+e^{\Delta_m-\Delta})(1+be^{\Delta_m-\Delta})}{b(1+e^{\Delta_m-\Delta})^2} \quad 6.1.7$$

which is symmetrical in $\pm (\Delta_m - \Delta)$ and represents a bell-shaped curve.

If Δ varies linearly with pressure, this bell-shaped curve is the expected result of a pressure experiment, as shown in Fig. 6.1.1 (a), and similar curves have indeed been found in Ge(71F1), peaking at 27 Kb where the $\langle 111 \rangle$ and $\langle 100 \rangle$ bands are both populated.

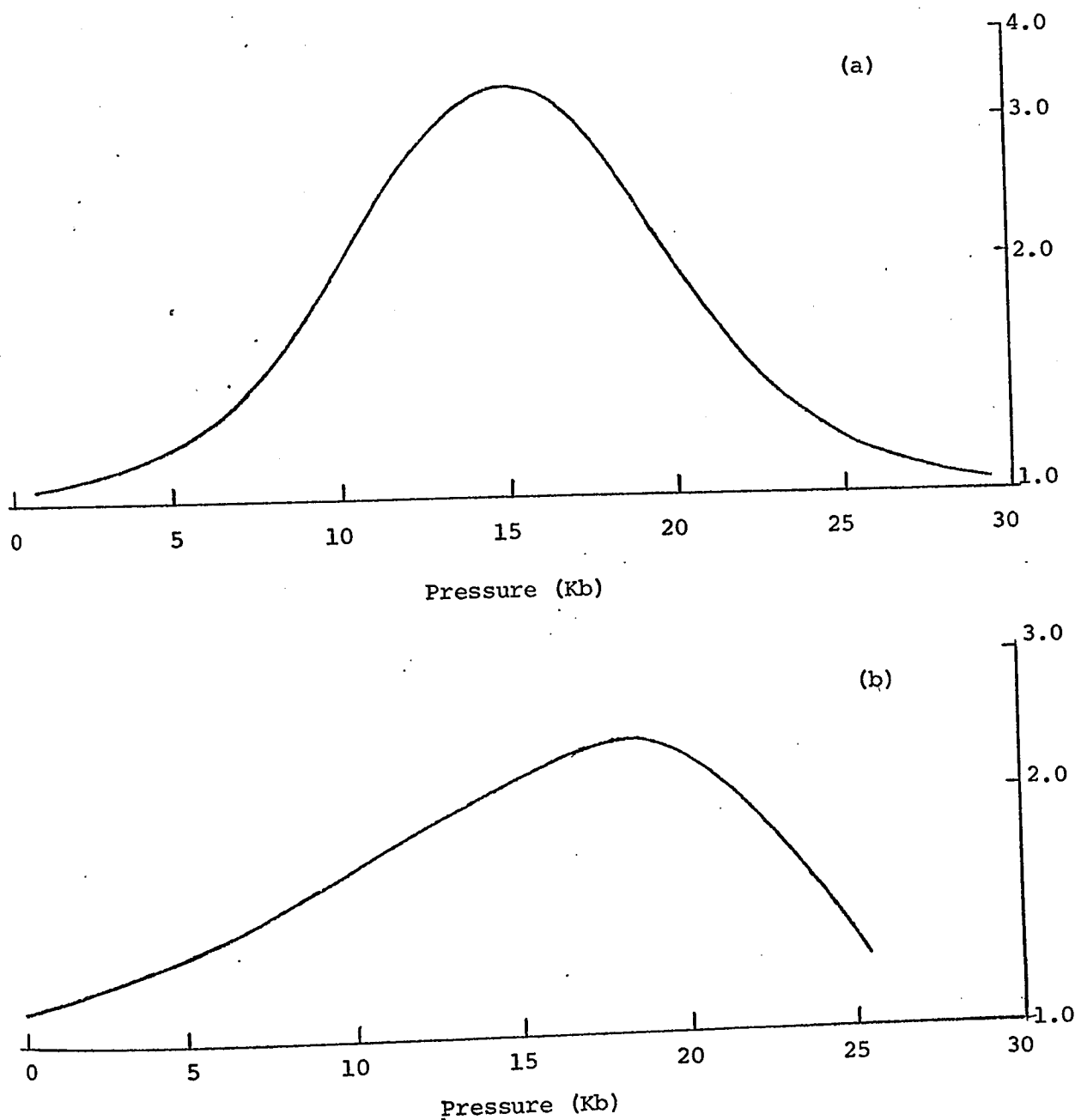


Figure 6.1.1 (a) Theoretical variation of Hall coefficient with pressure according to elementary two-band model, assuming a constant mobility ratio of 10.

(b) Composite experimental result for alloys containing GaSb, to same pressure scale as (a) but with arbitrary origin.

The present work did not provide complete bell-shaped curves for any specimen, but in the spirit of the above approximations one may assemble a composite bell-shaped curve by sliding each experimental curve both horizontally and vertically so as to optimize the fitting together of different curves. Fig. 6.1.1 (b) shows the result of doing this with the experimental curves of Figs. 5.2.2 and 5.2.4. Although the curves did not fit together perfectly, especially where different electron concentrations were involved, there was no difficulty in drawing the composite result, which is interesting since it shows a distinct forshortening on the high-pressure side of the maximum, an effect which is also noticeable on the individual curves.

The principal cause of forshortening of the individual curves is the decrease of the $\langle 000 \rangle$ band mobility with pressure as predicted by the detailed analysis which follows. By contrast, the symmetrical nature of the cited Ge result indicates that the $\langle 111 \rangle$ and $\langle 100 \rangle$ mobilities remain constant.

Construction of the composite curve does not require the assumption of any general equivalence between the composition and pressure variables. As emphasized by Bassani and Brust (63B1) there is no general equivalence. It is only necessary to assume that : (i) the Hall coefficient variation is determined primarily by ΔE , and (ii) the pressure coefficient of ΔE is similar for all the specimens.

Values of Parameters

Few of the required parameters have actually been measured on the alloys. Of those which have been, the most significant are the direct band gaps, their temperature dependences, and the central band shapes (effective masses). Data for all of these has been summarized in Section 4.1, where a working basis for their pressure dependences was also formulated from a combination of theoretical arguments and interpolations from values for the compounds.

The $\langle 111 \rangle$ band effective mass m_2^* is not well known in III-V materials, and the Ge value of 0.22 is often assumed. Van Tongerloo and Woolley (69T2) obtained the value 0.226 for GaSb, and this value was used for all specimens; if the true value were (say) $m_2^{*'}$, ΔE would be in error by only a small amount: i.e. $k_B T \ln (m_2^*/m_2^{*'})^{3/2}$. For the ellipticity K , Piller's value (64P1) of 8.6 in GaSb was used; the value is not critical.

Compensation by acceptors is significant in n-type GaSb, since undoped material is always p-type. According to Baxter et al (67B1) the acceptors become doubly-charged in n-type material, and therefore yield four-fold scattering effect, (Section 4.2). Since the experimental quantity in n-type material is not the donor density N_D but the total electron density n_t , (itself deduced from n_H by two-band analysis), the effective charged centre concentration for scattering is;

$$N_{cc} = n_t + 6N_A^{--} + n_2$$

6.2.3.

which allows for the effects of compensation and for scattering by $\langle 111 \rangle$ electrons. A survey of undoped ingots prepared in this laboratory showed that material containing more than about 60% GaSb would be p-type, and for lower GaSb content the material would be n-type with about 10^{16} extrinsic electrons per cm^3 . From these observations, the double-acceptor densities were assumed to be 10^{17} cm^{-3} in 100% GaSb, tapering exponentially to one-tenth of this at 60% GaSb. Certain other parameters are known in the unalloyed compounds; and values for the alloys may be deduced by linear interpolation; these include the low and high frequency dielectric factors and the optical phonon energy $\hbar\omega_l$. The values collected by Rode (70R1) were used, as listed in Table 6.2.A.

TABLE 6.2.A. PARAMETERS FOR III-V COMPOUNDS.

	GaAs	GaSb	InAs	InSb
κ_0	12.9	15.0	14.55	18.7
κ_∞	10.92	13.8	11.78	16.76
$\hbar\omega_l (\text{eV})$	0.0362	0.0299	0.0302	0.0240

The amount of alloy scattering as predicted theoretically was thought to be too high since the theoretical $\langle 000 \rangle$ mobilities then turned out to be somewhat lower than those obtained from two-band curve fitting on the most symmetrical (higher mobility) specimens of $\text{Ga}_x\text{In}_{1-x}\text{Sb}$.

having x in the range 0.8 to 0.95. Therefore the contribution, predicted by eq. 4.2.15 was arbitrarily reduced to one half for all calculations, the remaining contribution being then about 10% of the total scattering in the above specimens. From this small value, and the fact as discussed later that eq. 4.2.15 does not explain the large variation with pressure as observed in specimens showing primarily only $\langle 000 \rangle$ band transport, it remains uncertain whether alloy scattering has been properly understood or whether it is significant.

6.2 ANALYSIS OF SPECIMENS CONTAINING GaSb

Outline of Detailed Procedure.

For the numerical work a computer program was developed, based on previous methods used by Coderre (69C3) for locating the Fermi level in multiband, non-parabolic situations. This method uses eqs. 4.1.17 and 4.1.22, with the aid of a table of Fermi integrals.

In prior work on GaSb the pressure data were analyzed assuming a constant $\langle 000 \rangle$ mobility μ_1 , and the $\langle 111 \rangle$ mobility μ_2 was usually assumed constant also, except that Pitt (69P1) took the resistivity increase between 15Kb and about 20 Kb to indicate a small decrease in μ_2 . This conclusion is dubious, since the resistivity data presented in (69P1) is consistent with a constant mobility μ_2 if all three conduction bands are allowed for simultaneously.

In the present work μ_2 was taken as constant, at a value which was chosen for best fit to the data on each specimen. The relevant

scattering mechanisms have not been clearly identified in the $\langle 111 \rangle$ band of any III-V compounds; Hilsum (64H1) gave some rough estimates in this regard, and Basinski (72B1) found that the temperature dependence of μ_2 in GaSb was consistent with scattering by a combination of acoustic phonons and charged centres. Whatever the scattering mechanisms may be, there was no reason to expect a significant pressure dependence in μ_2 .

On the other hand, there was good reason to expect μ_1 to decrease appreciably with pressure, from the combined effects of the increase in effective mass (see Section 4.1), the transfer of electrons into the $\langle 111 \rangle$ band where they become effective scattering centres, the decrease in average electron energy in the $\langle 000 \rangle$ band as it becomes depleted, and the increase in interband scattering as the band separation energy decreases.

The expressions for electron scattering given in section 4.2 were developed (in cooperation with J. Basinski) with the object of calculating the pressure dependence of μ_1 from theory, and then by fitting to the data, to establish the relative importance of different scattering mechanisms. By fitting the data more closely than could be achieved on the assumption of a constant μ_1 , the value of the band separation energy ΔE could be more accurately determined on each specimen, and as a by-product, it was hoped to determine the value of D_{12} the interband scattering parameter.

Some preliminary curve fitting was done using various empirical relations for the pressure dependence of μ_1 . Of these, the most favoured was the assumption that μ_1 varied as $(E_G^*)^\gamma$, the exponent γ being chosen for best fit to the data. This has a physical basis in the interrelation between E_G^* , m_0^* and μ_1 , and each of the scattering mechanisms except the interband scattering can be characterized by a value of γ . However, as discussed later, the empirically-chosen γ was usually higher than any to be expected theoretically.

For detailed curve fitting the GaSb data was a convenient starting point, since its parameters were better known, and because good initial values of μ_2 could be found from the asymptotic values of the resistivity ρ and Hall coefficient R_H at higher pressures. For alloy specimens the values of μ_2 were obtained in a similar way, but with lower accuracy with diminishing GaSb content since the electron transfer was even less complete at maximum pressure. At the same time, the importance of μ_2 diminishes, and for compositions where the Hall maximum was not reached at highest pressure the dominant effect is the loss of electrons from the high-mobility $\langle 000 \rangle$ band.

The analysis of GaSb-rich alloys was complicated by the resistance barriers, which obscured the absolute values of the mobility in many specimens. However, as discussed in Section 5.2, highly asymmetric specimens were found to show pressure behaviour which was entirely compatible with others of similar composition which were selected to avoid barriers.

For curve fitting, the adjustable parameters were: the band separation ΔE , the total electron concentration $n_t = n_1 + n_2$, the mobility

ratio $b_0 = \mu_1/\mu_2$ for low pressure, the averaging parameter r_2 for the $\langle 111 \rangle$ band, and parameters representing μ_1 and its pressure dependence. Using the empirical mobility variation, these were: a low-pressure value $\mu_1(0)$ and the exponent γ . Using the detailed scattering theory, the parameters were: D_{12} for interband scattering, and N_{cc} the effective number of charged scattering centres. N_{cc} could be regarded as determining N_A^{--} , but not with assurance, since there are various uncertainties in the theory, such as the Born approximation, and the efficiency of scattering by the drifting and not "infinitely heavy" $\langle 111 \rangle$ electrons. The averaging parameter r_1 was also calculated from theory at each pressure when the detailed calculation of μ_1 was performed; when the empirical μ_1 variation was assumed, a nominal value of r_1 close to unity was taken.

Results of curve fitting

Following the procedure which has been described, it was found that the pressure dependences of the two GaSb specimens could be well fitted (see Figs. 5.2.1. and 5.2.2.) by choosing a value of D_{12} of 5.5×10^8 eV/cm in both cases, and using the same value of 0.087 eV for ΔE as determined by Basinski (72B1). The contribution of interband scattering to the values of μ_1 was only about 8% at low pressure in both cases, but the resulting increase in scattering with increase of pressure was important in shifting the maxima in the Hall curves to lower pressures. In order to impose agreement between the experimental apparent mobilities μ_H and those calculated from the scattering theory combined with two-band analysis, the values of N_{cc} calculated from eq. 6.2.3 were reduced by

10% in both cases. As earlier pointed out, this need not be regarded as determining values of N_A^{--} lower than the assumed value of 10^{17} cm^{-3} , but if this conclusion were drawn, the revised values of N_A^{--} would be 0.8 and $0.5 \times 10^{17} \text{ cm}^{-3}$ respectively.

In view of the uncertainties in the absolute values of μ_H in those alloy specimens containing appreciable barriers, the values of N_{cc} for the alloy specimens were not individually adjusted, but were arbitrarily set 10% lower than the predicted values, in conformity with GaSb. As already discussed, the alloy scattering was arbitrarily reduced to one half of that defined by eq. 4.2.15. Values of ΔE , b_o and D_{12} were adjusted for best fit to the pressure dependence of each specimen, and the total electron concentration n_t was adjusted to impose agreement with the observed Hall coefficient at low pressure. A value of 1.3 ± 0.05 for the averaging parameter r_2 was found to give best fit to the GaSb-rich specimens, and had insignificant effect on the others.

With decreasing GaSb-content an increasing value of D_{12} was required, and a poorer fit obtained, as shown by the smooth curves in Figs. 5.2.1 to 5.2.4. For specimens containing less than about 80% GaSb no values of D_{12} could explain the rapid increase in resistivity with pressure. Using the empirical form of the mobility variation, the results shown by the dotted curves in Figs. 5.2.1 to 5.2.4 were obtained. The GaSb specimens were also fitted, but this is not shown since the curves overlap the smooth curves. Improved agreement was obtained with the

Hall dependences, using the same values of ΔE as used for fitting by the scattering theory, but the resistivity dependences are then less well fitted in many cases. However, the empirical mobility did provide a fit to the specimens containing less than 80% GaSb. (This of course in no sense explains the rapid decrease in mobility with pressure, but obtaining such a fit increases the confidence which can be placed in the determined values of ΔE .) The essential difference between the empirical mobility and that predicted from the scattering theory is that the former varies roughly linearly with pressure; on the contrary, the theoretical variation is small on the low pressure side of the Hall maximum, but then increases rapidly as electrons increasingly occupy the $\langle 111 \rangle$ band and become scattering centres, as the degeneracy decreases in the $\langle 000 \rangle$ band, and especially as the interband scattering becomes significant.

It may be worth noting that closer agreement could be obtained by choosing different values of the mobility ratio b_0 for the resistivity and Hall curves. This was discovered accidentally as the result of an error in the allowance for ellipticity; by coincidence the same error appears in ref. 69C4, where the expressions for conductivity and Hall coefficient are incompatible. The expression for conductivity agrees with eq. 4.3.1, but the expression for Hall coefficient, although entirely correct in itself, involves the ellipticity in such a way that for compatibility the conductivity expression also should involve the ellipticity explicitly. The result of not doing so is roughly equivalent

to taking b_0 for the resistivity as about 1.4 times the value assumed for the Hall coefficient, coupled with a reduction in the value of r_2 to about 1.0. It should be noted that the expressions are correctly given in ref. 69C3. It should also be noted that the erroneous fitting produced almost identical values of ΔE .

With the choice of parameters discussed above, the theoretical values of μ_H were usually distinctly higher than the measured values, for which the resistance barriers can be held responsible in most cases. In a few cases, the measured mobilities were higher than those calculated. The most significant of these is no. 18, where the values were 7280 and 6590 cm^2/vs respectively. This could be taken as evidence against a significant contribution by alloy scattering, but in view of the uncertainties in the dominant charged-centre scattering it is not possible to be definite.

Curve fitting was also applied to the two highly asymmetric specimens shown in Fig. 5.2.5. Although these specimens should be regarded as unreliable, the closeness of fit and values of parameters were found to be fully comparable with those of symmetrical specimens. Table 6.2.B lists the results obtained by curve fitting, using both the empirical variation of mobility and the scattering theory in cases where both methods were used. Not listed are the values of the averaging parameters r_2 and the effective impurity concentration N_{cc} , which have been sufficiently discussed above. The listed values of r_1 are the values calculated for low pressure. With increasing pressure the values decreased

TABLE 6.2.B

Values of ΔE , n_1 , n_2 , b_0 , γ and D_{12} determined by curve fitting, and theoretical low-pressure values of r_1 , μ_1 , μ_H obtained by imposing agreement with GaSb.

list #	x		ΔE (eV)	n_1 (10^{18} cm^{-3})	n_2 (10^{18} cm^{-3})	b_0	γ	D_{12} (10^8 eV/cm)	r_1	μ_1 (cm^2/Vs)	theor. μ_H
1	/	GaSb	.087	.139	.267	7.25		5.5	1.07	4100.	3610.
2	/		.087	.427	3.77	7.85		5.5	1.02	3770.	3020.
3	.012	GaAs _x Sb _{1-x}	.090	.420	1.06	9.30	3.6	6.5	1.03	3690.	3100.
4	.024		.093	.451	1.22	10.5	4.2	7.4	1.05	3690.	3230.
5	.062		.132	.935	.916	10.9	4.6	10.	1.08	4060.	4060.
6	.110		.159	1.18	.623	9.85	4.0	10.	1.07	4730.	4820.
7	.130		.175	1.47	.524	10.7	3.7	10.	1.06	5040.	5150.
8	.275		.260	2.37	.085	20.6	3.6	/	/	/	/
9	.345		.283	2.68	.049	20.4	4.0	/	/	/	/
10	.36		.294	2.51	.025	25.	3.0	/	/	/	/
11	.96	Ga _x In _{1-x} Sb	.121	.277	.190	10.0	4.8	8.	1.09	5110.	5190.
12	.96		.121	.722	.895	10.8	4.2	8.	1.06	4200.	4020.
13	.92		.131	.825	.835	13.4	4.2	9.	1.08	4550.	4570.
14	.89		.154	1.05	.688	14.1	4.0	10.	1.09	5030.	5190.
15	.88		.16	.165	.242	13.6	4.0	10.	1.09	7660.	8030.
16	.855		.171	1.33	.731	15.3	3.2	10.		5140.	5340.
17	.81		.21	.276	.008	8.75	/	10.	1.08	9860.	9480.
18	.805		.230	1.82	.211	20.	2.2	10.	1.04	5900.	6590.
19	.58		.367	3.44	.048	10.	2.4	/	/	/	/
20	.38		/	.286	/	/	2.5	/	/	/	/
21	.21		/	.464	/	/	1.3	/	/	/	/

towards unity, in consequence mainly of increased interband scattering. Similarly the values of μ_1 are listed to illustrate the values predicted theoretically for low pressure. The polar-optical contribution was about 15% for GaSb and most other specimens; the interband contribution was about 8% in GaSb at low pressure, and progressively less than this with diminishing GaSb content. This percentage increased with increasing pressure, but it should be recalled that the charged centre scattering also increases with pressure, so the relative increase in interband scattering is less pronounced than it otherwise would be. Several estimates were made of electron-electron scattering in GaSb and typical alloys, using Fig. 4.2.1 and eq. 4.2.18. In GaSb the amount seems to be small since the $\langle 000 \rangle$ electrons must encounter many more collisions with the more numerous $\langle 111 \rangle$ electrons, the donors, and the doubly-charged acceptors. The weighting factor α of eq. 4.2.18 should thus be approximately given by n_1/N_{cc} or about .08 for specimen no. 1. The reduced Fermi energy η is close to zero for this specimen, so for $s \approx 1$ the value of ϕ_{ee} should be about 0.7. The mobility reduction to be expected was thus only about 2.4%. For decreasing GaSb content the factor α increases steadily, but ϕ_{ee} moves closer to unity, so the e-e scattering remains small. In view of the other discrepancies between theory and experiment, there would be no point in pursuing the e-e scattering any further.

Discussion of results on specimens containing GaSb

In Figs. 6.2.1 and 6.2.2 the values of ΔE obtained from curve fitting and listed in Table 6.2.B have been combined with the known values of E_G as given by eq. 4.1.11 for both alloy systems, to show

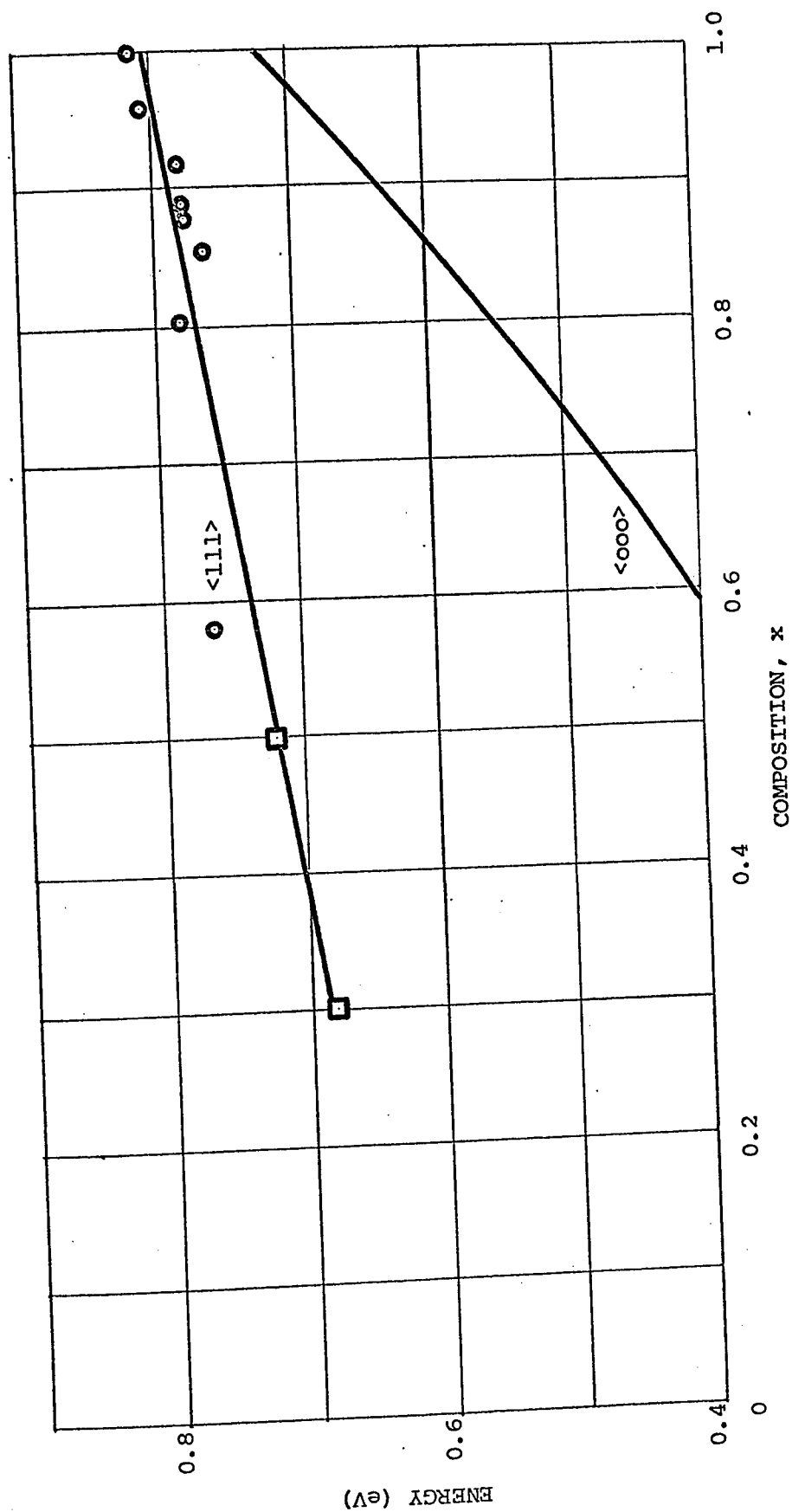


Figure 6.2.1 Band energies in $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ relative to valence band maximum.

Curves: from temperature dependence of resistivity and Hall coefficient, (69C4); points: circles (present work) and squares (69L1) are from pressure data.

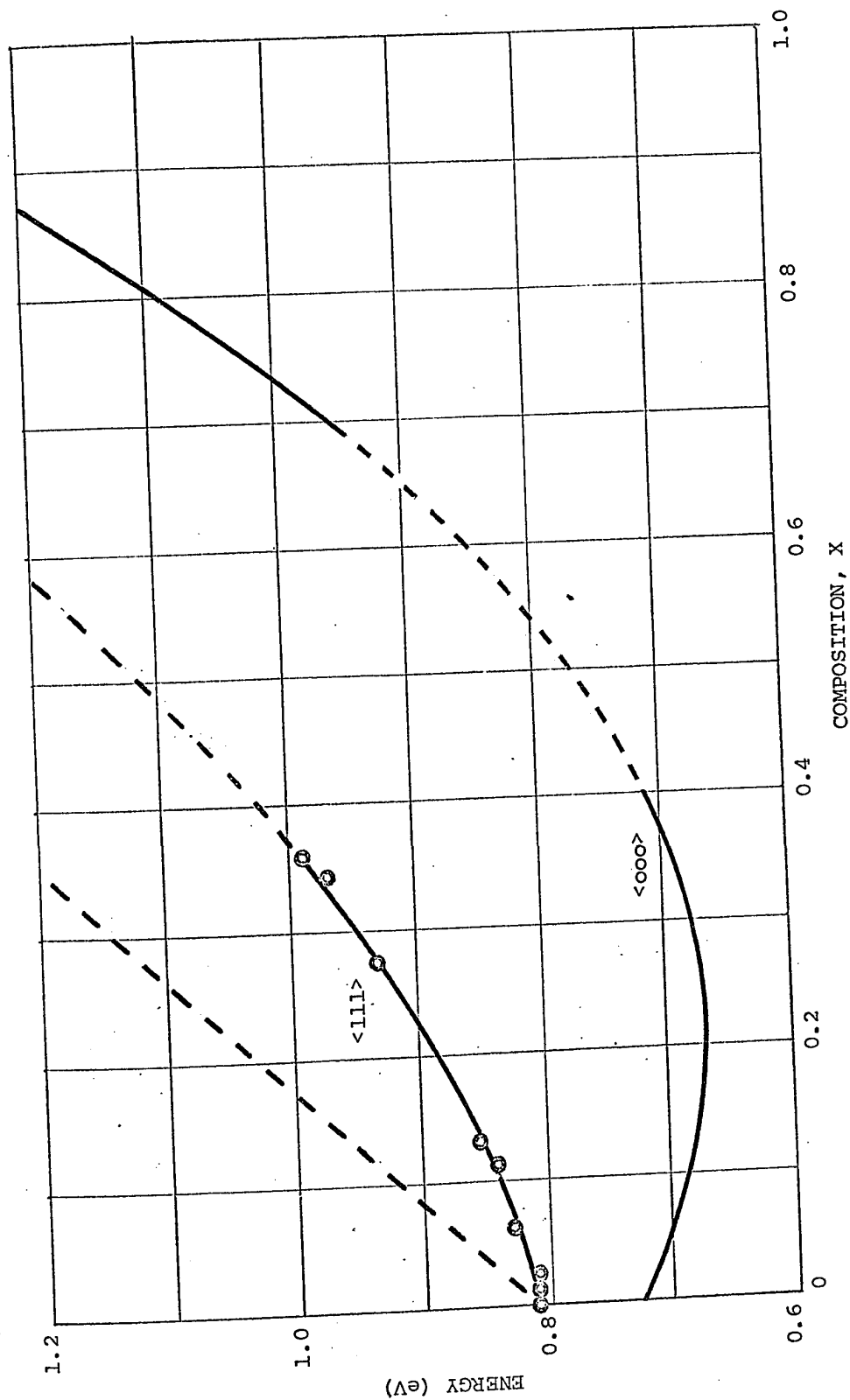


Figure 6.2.2. Band energies in $\text{GaAs}_x\text{Sb}_{1-x}$ relative to valence band maximum.

$\langle 000 \rangle$ curve: optical data (70T2); circles and $\langle 111 \rangle$ curve: pressure data, (present work); dashed straight line: linear interpolation between GaSb and GaAs.

the energies of the $\langle 000 \rangle$ and $\langle 111 \rangle$ conduction band minima relative to the valence band maximum.

The smooth curves A and B in Fig. 6.2.1 represent the $\langle 000 \rangle$ and $\langle 111 \rangle$ band energies as a function of composition in $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ as determined by Coderre and Woolley (69C4) from resistivity and Hall data at higher temperatures. The circles represent the present results, and the two squares represent values determined by Lorenz et al (69L1) as discussed in Section 5.2.

All these results are in reasonable agreement with each other, except for the circle representing $x = 0.58$ (specimen no. 19). The uncertainty in determining ΔE from curve fitting was larger for this specimen, partly because the two-band effects are only just becoming apparent at 12Kb, but even more because this specimen was heavily doped: ($3.3 \times 10^{18} \text{ cm}^{-3}$), and with so many carriers crowded into the $\langle 000 \rangle$ band the analysis relies heavily on the Kane model (specifically eq. 4.1.22) for locating the Fermi level. Inspection of Fig. 4.1.1 indicates that for this electron concentration the use of eq. 4.1.22 in place of the Kane equation itself might cause the Fermi level to be set too high by as much as 0.025 eV, which would explain the discrepancy. At such concentrations, the Kane equation itself should of course be regarded with caution. The two results of Lorenz et al should on the other hand be reliable, since these specimens were undoped and had carrier concentrations of only 10^{15} cm^{-3} approximately. As a test of consistency between the method of analysis used by these workers and the present calculations the pressure dependence for $x = 0.5$ was analyzed using

the same parameters as presently assumed, and the resulting value of E was in complete agreement with the value quoted by Lorenz et al. The value for $x = 0.3$ could not be checked since the pressure dependence was not given.

The scatter among the other points on Fig. 6.2.1 may perhaps be caused by errors in the determination of composition, since this was measured on material adjacent to the specimens from the same ingot cross-sections. The specimens themselves were saved for possible use in other measurements. It should be observed that an error in composition would translate a point parallel to curve A in Fig. 6.2.1, rather than horizontally; therefore the errors which must be assumed in order to reconcile all the points except that for $x = 0.58$ would be $\pm 2\%$.

Turning now to Fig. 6.2.2 representing the system $\text{GaAs}_x\text{Sb}_{1-x}$, there are no prior values of ΔE to be superimposed on those reported here; therefore the smooth curve B has been drawn for the best satisfaction of these alone. The straight line C has been drawn to connect the position of the $\langle 111 \rangle$ band in GaSb with the lowest position that this band may have in GaAs, viz. 0.38 eV above the central band. (Its actual position has been a matter of dispute.) Curve B shows a marked deviation from line C, which may be the first definite evidence of distinct "bowing" in a band energy vs. composition relation for other than the $\langle 000 \rangle$ band, and should be of interest to those concerned with the band theory of alloys.

It should also be stated that the value 0.087 eV for ΔE in GaSb is that determined by Basinski (72B1), and this value was chosen so as to make the results as compatible as possible. By changing other parameters slightly it was found possible to fit the data using lower values of ΔE down to about 0.083 eV. Sagar (60S1) chose the value 0.074 eV when analyzing his pressure data; this is easily explained by his assumption of constant mobility μ_1 , which made a close fit to the data impossible.

Concerning now the mobility calculations, the $\langle 000 \rangle$ band mobility in GaSb has been satisfactorily explained in magnitude and pressure dependence at room temperature. In cooperation with J. Basinski and in agreement with the results of his magnetoresistance and Hall determinations at elevated temperatures, it has been found that the charged centre scattering predominates, with smaller contributions from polar optical phonon scattering, both intraband and interband. To explain the pressure dependence requires that the interband coupling coefficient D_{12} be set between 5 and 6 times 10^8 eV/cm, compared to Basinski's value of 3.6×10^8 eV/cm. This seems reasonable agreement when it is recalled that prior attempts to determine the amount of interband scattering from pressure data (e.g. 71F1) or otherwise have given only order-of-magnitude results.

Very little can be stated with confidence concerning the scattering mechanisms in the alloy specimens. The absolute value of the mobility μ_1 in those specimens where this could be determined is consistent

with the theoretical prediction that the charged-centre scattering predominates as in GaSb, with smaller contributions from polar optical phonons and possibly alloy scattering. The theory fails however to explain the rapid decrease of μ_1 with pressure which is required to explain the pressure data using two-band analysis. The resistance barriers cannot be responsible, since the rapid variation in μ_1 was found even in compositions for which no barriers existed (e.g. specimen no. 19), and as already discussed, specimens showing severe barriers (i.e. high asymmetries and low apparent mobilities) showed fully consistent pressure results with specimens of similar composition which were selected so as to avoid barriers. The pressure data of Lorenz et al on lightly-doped $\text{Ga}_{0.5}\text{In}_{0.5}\text{Sb}$ may be significant in this regard. The resistance in that specimen showed only moderate pressure dependence in the region of single band conduction, suggesting that the rapid variation is associated in some way with high impurity concentration. One might expect the dopant to distribute itself according to the random microscopic fluctuations in composition, if the segregation coefficient of the dopant depends on alloy composition. This would change the nature of the scattering radically, but at present there is no reason to expect such scattering to be more pressure dependent.

6.3 DISCUSSION OF SPECIMENS CONTAINING InAs

The invariance of the Hall coefficient with magnetic field in undoped InAs indicates that the averaging parameter r was close to unity, as expected for polar-optical scattering, and renders unlikely the possibility that the increase with pressure could be due to r increasing. Most likely, the increase of the Hall coefficient with pressure is due to the freezing out of electrons onto deep impurity levels. If so, the relative pressure coefficient between the conduction band and the deep levels would be about 7.0 meV/Kb.

Heavily-Se-doped InAs was investigated because Kwan and Woolley (68K3) had found evidence of two-band conduction in similar material. This evidence was apparently clear: the transverse magneto-resistance varied linearly as B^{-2} in several specimens, as it also does in GaSb, (72B1). Whether the second band had $\langle 111 \rangle$ symmetry, as assumed in (68K3), or $\langle 100 \rangle$ symmetry, we would expect the resistivity and Hall coefficient to vary substantially with pressure, due to electron transfer between bands. As Fig. 5 shows, the uncorrected Hall coefficient remained constant within the experimental scatter, which was larger than usual because the apparatus was not well suited to measuring the small potentials found in heavily-doped specimens. A trend of 2% would have been noticeable; if anything, there was a decrease of perhaps 1%, which is the amount to be expected from dimensional compression. The two pressure runs terminated at 7.5 Kb because of leaks, but provide evidence

that all electrons were in the central band at room temperature and pressure. The possibility that two bands were populated but had closely-matched pressure coefficients is highly unlikely, since a relative shift of only .0025 eV would change the population in the upper band by about 10%. The possibility of close matching between the mobilities seems equally unlikely. The 7% observed increase in mobility is smaller than that found in the undoped specimens; this is to be expected, since the Fermi level will be high in the conduction band, where the effect of pressure on the effective mass will be greatly diminished. The absence of a pressure dependence in the Hall coefficient suggests reconsideration of the magneto-resistance results. These could be due to pronounced fluting of the conduction band at higher energies close to the Fermi level, implying a distribution of effective masses at this energy. The fluting may be insensitive to pressure, so that the relative numbers of light and heavy electrons may remain constant while the average mass increased slightly, in conformity with the resistivity increase. The three measurements on $\text{InAs}_x\text{Sb}_{1-x}$ will not be discussed in detail, since additional measurements have recently been made by M. Gratton of this laboratory, covering the complete alloy range, in good agreement with those presented here. It is not yet certain if the observed increases in Hall coefficient can entirely be explained as due to freeze-out of an intrinsic contribution, or if a deep impurity should be postulated, as in InAs.

Turning finally to the two $\text{Ga}_x\text{In}_{1-x}\text{As}$ results, the resistivity increase is about as expected for material having these band gaps, noting that GaAs and InAs appear to have rather smaller pressure coefficients than GaSb and InSb, (Section 4.1). Specimen no. 30 shows a 2% decrease in uncorrected Hall coefficient, which is just the amount to be expected when allowance is made for dimensional compression. On the other hand, specimen no. 29 appears to remain constant. In both cases, the experimental scatter is less than 1%, so that this lack of consistency remains as a minor discrepancy.

7. SUMMARY AND CONCLUSIONS

Alloy Preparation

It has been shown that the growth of III-V alloys in bulk form from stoichiometric liquids using the new technique of sequential growth produces material in the most convenient form for many research purposes. Despite the fact that such material is usually polycrystalline, the uniformity of composition is a great advantage which is not found when similar (highly segregating) materials are deposited epitaxially onto substrates consisting of one of the alloy constituents. Furthermore, the composition profiles are sufficiently tapered as to provide a wide range of compositions in each ingot, which is a significant advantage in view of the many weeks needed for growth if the ingot is to be homogeneous.

The practical aspects of sequential growth have been described in sufficient detail that this technique could be readily applied by others who may be interested. A workable theory for the process has also been presented, and shown to provide at least qualitative guidance. Discrepancies between the predicted and measured composition profiles remain, and serve as a warning perhaps that the theoretical ideas have been oversimplified.

It has also been shown that the incorporation of Te dopant into GaSb-rich ingots gives rise to severe resistance barriers at any irregular grain boundaries which may be present, but not at twin boundaries. This observation fully explains the anomalously low apparent mobilities previously reported for such materials at room temperature. By growing ingots under improved conditions yielding larger crystallite size it was

possible to select specimens by potential mapping in such a way as to avoid barriers, and in such cases the apparent mobilities are in good agreement with those deduced by extrapolation from high temperatures (69C4), and with the detailed scattering calculations.

Analysis of electron transport data under hydrostatic pressure

The most significant outcome of this work has been the determination of the band separation ΔE as a function of alloy composition at room temperature and pressure in the systems $\text{GaAs}_x\text{Sb}_{1-x}$ and $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ towards the GaSb-rich side. The results are in good agreement with prior data of Coderre and Woolley (69C4) and of Lorenz et al (69L1) in the latter system; no prior results are known for the former system.

Had greater pressures been available, ΔE could have been determined for InSb-rich compositions also, although the two pressure determinations of McGroddy et al leave little room to doubt that the variation of ΔE is as shown in the figure.

A secondary outcome has been to show (in cooperation with J. Basinski, 72B1) that the mobility in GaSb at (and above) room temperature can be explained in terms of charged-centre scattering as the principal mechanism, with small but significant contributions from intraband and interband scattering by polar-optical phonons. In agreement with similar conclusions by Baxter et al. (67B1), which were based primarily on measurements at 70°K, the mobility in GaSb should no longer be regarded as being anomalously low. The pressure dependence is best fitted by taking a value of $5.5 \times 10^8 \text{ eV/cm}$ for D_{12} .

the interband scattering coefficient. This differs from the value 3.6×10^8 eV/cm deduced by Basinski, but both values are well within the range 10^8 to 10^9 eV/cm within which D_{12} is believed to lie in GaAs, (68C2). The value of 5.5×10^8 eV/cm should be regarded cautiously, since it depends upon a correct assessment of the pressure dependence of the charged centre scattering.

The work on InAs and its alloys has played a minor role in this study, and the discussion of Section 6.3 leads to only one significant conclusion, namely that the electrons in InAs appear to be confined to a single band even at concentrations as high as $6 \times 10^{19} \text{ cm}^{-3}$. This contradicts the interpretation placed on magnetoresistance measurements in similar material by Kwan and Woolley (68K3), but agrees with recent analysis of thermo-reflectance data by R. Senechal in this group.

Suggestions for Future Work.

Many proposals could be made for filling in gaps in the range of materials prepared, and in the measurements performed. The gaps arose from various false starts and early misunderstandings; many of these will be obvious from the forgoing accounts, and only a few major points need be enumerated here. The technique of sequential growth was left in a somewhat untidy condition; preferably a few more ingots should have been prepared to demonstrate the value of using both forward and reverse zone passes at the proper low speeds. The possibility of preparing ingots having composition profiles tapering smoothly over the entire composition range should have been demonstrated in practice,

instead of leaving this to be inferred from results (on $\text{Ga}_x\text{In}_{1-x}\text{Sb}$) which were less than perfect. Less dopant could have been used in many cases, since the larger amounts used in the materials selected for pressure measurements were added with the intention of "swamping" the resistance barriers. Not only was this not achieved, but the preparation of specimens free from barriers was in fact achieved by other means instead.

There is good reason to believe that sequential growth would be a useful technique for the preparation of other highly-segregating alloy systems, such as those containing AlSb, and perhaps also for quaternary systems. The most interesting materials for pressure work would be those containing GaSb. The sequential growth technique would of course not of itself solve the problem of the chemical reactivity of materials containing Al.

It would be of some interest to extend the transport measurements to higher pressures, even if this meant forgoing the Hall measurement and concentrating on the resistivity, as has been customary so often in the past.

It would be of equal interest to investigate the effect on the pressure behaviour of using lightly-doped specimens. In this way it should be possible to make progress on the understanding of transport in alloys containing GaSb.

Further investigation of pressure effects in the alloys containing InAs has already commenced, and should in due course lead to new conclusions. It would be of interest to extend the measurements on

heavily-doped InAs to higher pressures, and perhaps to repeat them on heavily-doped alloys of the system $\text{InAs}_x\text{Sb}_{1-x}$ at compositions near the minimum of the band gap. This would require further work in alloy preparation, but would appear not to require any new techniques.

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