

CONTRIBUTION FROM THE SPERRY RAND  
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at 73.5–75° while 2,4-diphenylborazine melts at 120–122°. 2,4,6-Triphenylborazine has already been described. It was identified by its melting point, 175–177° (reported 175–176°<sup>6</sup> and 183–185°<sup>7</sup>), and by its infrared spectrum.<sup>8</sup>

*Anal.* Calcd. for B<sub>3</sub>N<sub>3</sub>C<sub>6</sub>H<sub>10</sub>: B, 20.8; N, 26.8; C, 45.0; H, 6.43; active H for 2 B–H bonds per molecule, 1.27. Found: B, 20.4, 21.0; N, 26.0, 25.8; C, 48.8, 49.0; H, 6.36, 6.33; active H, 1.25.

*Anal.* Calcd. for B<sub>3</sub>N<sub>3</sub>C<sub>12</sub>H<sub>14</sub>: B, 14.0; N, 18.1; C, 61.9; H, 6.06. Found: B, 13.7; N, 17.9; C, 61.6; H, 6.16. The infrared spectra of samples of 2-phenylborazine and 2,4-diphenylborazine contained in KBr pellets are recorded in Table I and X-ray diffraction patterns of the two compounds are given in Table II.

TABLE I  
INFRARED SPECTRA OF 2-PHENYLBORAZINE AND  
2,4-DIPHENYLBORAZINE<sup>a</sup>

2-Phenylborazine		2,4-Diphenylborazine	
cm. <sup>-1</sup>	I/I <sup>0</sup>	cm. <sup>-1</sup>	I/I <sup>0</sup>
3470	m	3460	m
2500	m	2505	w
1600	m	1605	m
1500	sh	1510	m
1440	vs	1455	vs
1425	sh	1365	m
1375	m	1250	w
1335	m	1205	w
1220	w	909	m
1070	w	899	s
1000	w	772	w
895	s	708	s
769	w		
736	sh		
713	s		

<sup>a</sup> The symbols used to designate intensities are: s, strong; m, medium; w, weak; v, very; and sh, shoulder.

TABLE II  
X-RAY POWDER PATTERNS OF 2-PHENYLBORAZINE AND  
2,4-DIPHENYLBORAZINE<sup>a</sup>

2-Phenylborazine		2,4-Diphenylborazine	
d, Å.	I/I <sub>0</sub>	d, Å.	I/I <sub>0</sub>
10.2	m	6.21	vw
5.39	w	5.29	w
4.46	vs	4.91	m
3.97	s	4.54	vs
3.77	vw	4.11	s
3.38	vw	3.67	m
3.11	s	3.57	vw
3.08	vw	3.52	s
2.91	vw	2.89	vw
2.72	w	2.69	vw
2.60	w	2.21	vw
2.52	vw	1.97	vw
2.42	vw	1.82	vw
2.36	vw	1.66	vw
2.16	w		
2.08	w		
1.91	w		
1.70	w		

<sup>a</sup> The symbols used to designate intensities are: s, strong; m, medium; w, weak; and v, very.

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## Solid Solution in the Gallium Arsenide–Indium Arsenide System

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The occurrence of solid solubility in binary systems of III–V semiconductor compounds has been studied by a number of investigators. Some of the early results suggested that only limited ranges of solid solution could be obtained in the systems GaSb–InSb, GaSb–AlSb, and InSb–AlSb.<sup>1</sup> Goryunova and Fedorova<sup>2</sup> reported that a lengthy annealing period in the solid state was necessary to achieve a single phase in the GaSb–InSb system, although this was not adequate for homogenization of GaAs–InAs compositions. Subsequently it has been shown<sup>3–5</sup> that for most of the binary III–V systems it is possible to prepare reasonably homogeneous single-phase material provided that a sufficiently prolonged heat-treatment of the powdered solid is used, at a temperature not far below the solidus level. The feasibility of preparing massive (unpowdered) homogeneous products was discussed by Woolley and Smith.<sup>5</sup> They applied both zone recrystallization and directional freezing to an equimolar GaSb–InSb composition but in each case obtained a spread of composition across any given cross section of the ingot. The gradient freezing and zone leveling methods, using a traveling furnace, were applied to the GaAs–InAs system by Abrahams, Braunstein, and Rosi.<sup>6</sup> The zone leveling technique gave greater homogeneity across a given section of an ingot, and they reported composition spreads of <2% near the ends of the phase diagram. Woolley, Gillett, and Evans<sup>7</sup> subsequently described the preparation of GaAs–InAs samples by the directional freezing technique over the range 11–82 mole % GaAs. Above 82 mole % GaAs, prolonged annealing of solidified melts was used.

It is important to note that in all the above investigations the resultant materials were essentially polycrystalline, quite apart from any question of homogeneity.

The work now reported was intended to investigate the possibility of preparing GaAs, containing a small percentage of InAs in solid solution, in the form of single crystals of a usable size from the standpoint of physical measurements.

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### Experimental

The gradient freezing method was chosen as the preferred method of crystallization. This technique simplifies the provision of the requisite equilibrium vapor pressure of arsenic by means of an arsenic reservoir in a secondary furnace. Possible interference with the crystallization process by vibration arising from a traveling furnace is also avoided. Polycrystalline GaAs and InAs were used as starting materials. Mass spectrographic examination of the final product showed that at that stage impurities were all at the part per million level, except for the presence of silicon, 50 p.p.m., and tin, 30 p.p.m. There was about 300 p.p.m. of tellurium derived from the GaAs, which was highly doped n-type. A ratio of 98 mole % GaAs, 2 mole % InAs was used. The crystallization was carried out in a fused quartz boat 6 in. long and about 0.75 in. wide contained in an evacuated fused quartz tube. A small amount of arsenic was contained in a separate quartz boat at one end of the tube. A main furnace was used to heat the arsenide boat and a secondary furnace was provided around the arsenic boat to maintain the lower temperature (610°) necessary to give the required arsenic pressure.<sup>8</sup> It was necessary to ensure, in the usual way, that no point in the quartz tube was at a temperature less than 610°, while obtaining a suitable symmetrical temperature profile along the arsenide boat. The polycrystalline arsenide starting materials were used without conversion to fine powders so as to minimize contamination. Intimate mixing of the components was therefore impracticable and it was found important to place the InAs on top of the GaAs rather than in contact with the quartz boat. Otherwise the lower melting InAs could form a separate liquid phase during heating and this tended to increase the chance of adherence to the quartz.

The main furnace temperature was raised by means of a program controller at a rate of 200–300°/hr. to 1300°, as measured by a Pt vs. Pt + 10%Rh thermocouple attached to the outside of the quartz tube above the middle of the arsenide boat. When the temperature reached 800° the secondary furnace was switched on so as to raise the arsenic reservoir temperature to 610°. The arsenide temperature was held at 1300° for 10 min., lowered to 1270° over a period of about 10 min., and then cooled at a rate of 20°/hr. to 800°. The main and secondary furnaces were then switched off and allowed to cool to near room temperature at their natural cooling rates.

### Results

In general the above experimental procedure yielded ingots consisting of a number of single crystal regions, some of which were as large as 2 cm. × 1 cm.<sup>2</sup>. Impact fracture of an ingot produced good cleavages, which often served to delineate crystal boundaries. Semiquantitative X-ray fluorescence measurements indicated that crystals near the ends of the boat contained <0.5 mole % InAs and that higher concentrations occurred nearer the middle of the boat. This type of distribution is to be expected from the higher freezing temperature of GaAs with respect to InAs and intermediate ratios.

A portion of an ingot about 2 cm. long and 1 cm.<sup>2</sup> cross section and bounded by two parallel cleaved faces was studied in some detail in regard to crystallography and composition.

A series of X-ray Laue photographs was taken, with the beam incident at various points along the length of the specimen. Identical patterns were obtained in each case, consistent with the view that the sample

was a single crystal. Laue photographs of an end face showed that this had cleaved in a [110] plane. Calculation of interplanar spacing from diffractometer measurements yielded a unit cell size of 5.6627 Å. A corresponding determination for a [110] plane sample of GaAs gave a unit cell size of 5.6567 Å, *i.e.*, 0.006 Å smaller. According to Woolley and Smith<sup>4</sup> the lattice parameter varies linearly with molecular composition in the system GaAs–InAs and 1 mole % substitution of InAs increases the lattice parameter by 0.004 Å. The observed change of 0.006 Å, compared with GaAs thus corresponds to 1.5 mole % InAs.

### Discussion

It has been shown that GaAs–InAs solid solutions near the GaAs end of the system can be prepared in the form of large single crystals by means of a gradient freezing technique. In contrast, prior work on binary III–V compounds appears to have been confined to powdered or polycrystalline specimens. Single crystal semiconductor materials of this kind are of interest in achieving energy band gaps intermediate between those available in the end members of the binary systems.

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### Ethylmagnesium Ethoxide

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In the preparation of magnesium hydride by pyrolysis of diethylmagnesium at 200°, under high vacuum, Wiberg and Bauer<sup>1</sup> observed a small amount of a volatile organomagnesium compound. The authors formulated the product as ethylenemagnesium (MgC<sub>2</sub>H<sub>4</sub>) on the basis of the mass balance in the pyrolysis reaction and from the quantity of ethane evolved upon hydrolysis of the volatile material. We now have obtained evidence that this organomagnesium sublimate is essentially ethylmagnesium ethoxide. The results of elemental analysis were not in agreement with the values calculated for MgC<sub>2</sub>H<sub>4</sub> but correspond closely to those for C<sub>2</sub>H<sub>5</sub>MgOC<sub>2</sub>H<sub>5</sub>.

*Anal.* Calcd. for MgC<sub>2</sub>H<sub>4</sub>: C, 45.9; H, 7.69; Mg, 46.4; ratio C:H, 2:4. Calcd. for C<sub>2</sub>H<sub>5</sub>MgOC<sub>2</sub>H<sub>5</sub>: C, 48.8; H, 10.2; Mg, 24.7; ratio C:H, 2:5. Found: C, 48.3; H, 10.0; Mg, 24.1; ratio C:H, 2:4.97.

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