

$\text{CdAs}_2\text{I}$ , phase C and As coexist. Finally at still higher pressures only phase C and As are found.

Resistance measurements along the  $415^\circ\text{C}$  isotherm yielded a break in the curve of resistance versus pressure at 33 kbar. This is the boundary between the region where  $\text{CdAs}_2\text{I}$  is predominant with traces of phase C present, but no As, and the region where  $\text{CdAs}_2\text{I}$ , phase C and As coexist. This point on both isotherms is in good agreement with the previously proposed<sup>5</sup>  $\text{CdAs}_2\text{I/II}$  phase boundary. As in the case of  $\text{ZnAs}_2$  it is certain that what was previously thought to be the  $\text{CdAs}_2\text{I/II}$  boundary, is the present decomposition boundary. An experiment on the same  $\text{CdAs}_2$  as was previously used<sup>5</sup>, was made, where the  $\text{CdAs}_2$  was contained in a niobium capsule. The results were in perfect agreement with the present results.

Efforts to determine the exact composition of phase C were made, with less success. Mixtures of  $\text{Cd}_3\text{As}_2$  and As and mixtures of Cd and As did not react to yield pure phase C at all, when the mixtures had the expected CdAs composition. However, when the mixtures had a  $\text{CdAs}_2$  composition phase C was obtained, but with excess As present. Raising the temperature above the previously determined melting temperature produced a new quenchable phase D, with a diffraction pattern very rich in diffraction peaks. Table II presents a

summary of these efforts from the various starting compositions tried.

X-ray quantitative analysis<sup>9</sup> techniques proved less consistent than previously, and the results, although indicating a composition close to CdAs, are not considered reliable enough.

The products from certain high pressure experiments were tempered in a similar fashion to those of  $\text{ZnAs}_2$ . The tempering time was  $\sim 17$  hours and  $300^\circ\text{C}$  was found to be sufficient to produce the atmospheric pressure phases. A schematic representation of the relationships between the phases is presented in Fig. 6.

The diffraction pattern obtained for phase C (CdAs), was indexed using the method of DE WOLFF<sup>10</sup>, and yielded an orthorhombic cell with  $a_0 = 5.993 \text{ \AA}$ ,  $b_0 = 7.819 \text{ \AA}$ , and  $c_0 = 8.010 \text{ \AA}$ . Systematic absences showed the space group to be Pbcu. Details of the crystallographic work will be published<sup>7</sup>.

In an attempt to understand the relative stabilities phases C and D and therefore also phases A and B, the following experiments were made.  $\text{CdAs}_2$  was held at 10 kbar,  $900^\circ\text{C}$  for  $\sim 1/2$  hour, cooled slowly to  $\sim 600^\circ\text{C}$ , and was found to yield a glassy substance upon quenching to ambient. This is in agreement with earlier work at atmospheric pressure<sup>13</sup>. This suggests that phases D and B are the

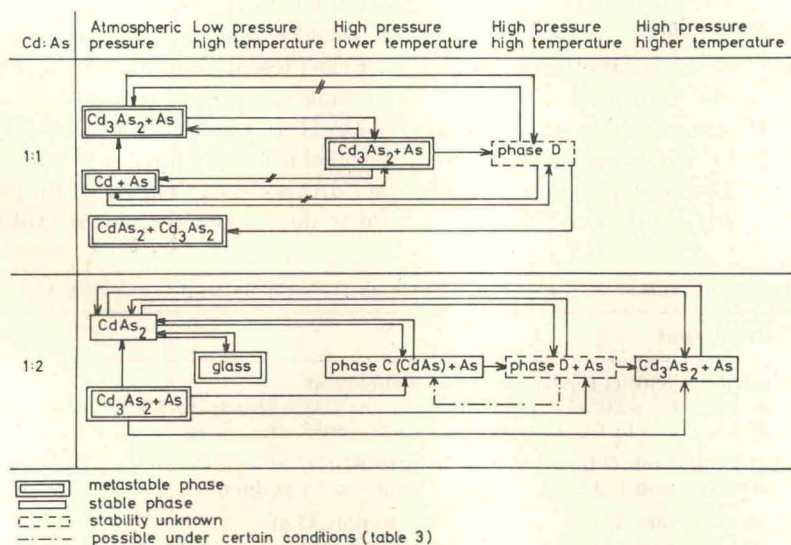


Fig. 6. Stability relationships between phases obtained from high pressures and high temperatures in the  $\text{Cd}_3\text{As}_2$ -As system.



products of the high pressure, high temperature region only. In the previous study<sup>5</sup>, an extra set of signals obtained in the high pressure region, were ascribed to the  $\text{CdAs}_2\text{II}$ -As eutectic. From the present results it is known that  $\text{CdAs}_2\text{II}$  does not exist. It is therefore tempting to assume that these signals belong to the  $\text{CdAs}$ -As eutectic, or that they are related to the melting of phase D, which is created when the melting temperature of phase C is exceeded for any length of time. This would tie in very well with the heating mechanism used to produce the double set of D.T.A. signals<sup>5</sup>. In the previous work it was noted that the strength of the lower signal (related to the amount of material present causing this signal), could be increased by spending more time above the melting temperature of phase C. The lower D.T.A. signal could be removed by lowering the temperature to  $\sim 25^\circ\text{C}$ . To relate this to the present work three results are presented in Table III. These results are in good agreement with the previous work, where only short periods were spent above the melting temperature. However, from the present results it appears that once phase D has been formed for longer periods of time, perhaps thereby destroying any seeding mechanisms present, the reverse transformation from phase D to phase C is not obtained. It is also possible that further change in composition occurs. A similar relationship between phases A and B is thought to exist.

### Discussion

From the present work it appears that what was previously<sup>5</sup> thought to be the melting curves of  $\text{CdAs}_2\text{II}$  and  $\text{ZnAs}_2\text{II}$  are probably the melting curves of  $\text{CdAs}$  and  $\text{ZnAs}$ . The phases B and D are thought to be metastable, and probably involve some process in the liquids of  $\text{CdAs}$  and  $\text{ZnAs}$ .

The phases  $\text{ZnAs}$  and  $\text{CdAs}$  are isostructural<sup>7</sup> with  $\text{ZnSb}$  and  $\text{CdSb}$ <sup>14</sup>. A recent paper on the phase diagram of  $\text{CdSb}$ <sup>15</sup> indicated a falling melting curve for  $\text{CdSb}$ , followed by a region above  $\sim 35$  kbar, where  $\text{CdSb}$  decomposes into  $\text{Cd}$  and  $\text{Sb}$ . Certain questions arise from this paper<sup>16</sup>. Above  $\sim 35$  kbar, the rising portion of the melting curve, is attributed to the  $\text{Cd-Sb}$  eutectic. An extrapolation of this curve to 1 bar, yields  $\sim 30$ – $50^\circ\text{C}$  for the metastable eutectic temperature. However, an estimate of the metastable eutectic temperature from the composition-temperature phase diagram, yields a value of  $\sim 150^\circ\text{C}$ . Although these values come from long extrapolations, the lack of agreement is noticeable. Furthermore, the  $\text{SbII/III}$  transformation causes a sharp break in the melting curve of  $\text{Sb}$ . Correspondingly there should be a slope change in the  $\text{Cd-Sb}$  eutectic temperature at  $\sim 65$  kbar where the  $\text{Cd-SbII}$  to  $\text{Cd-SbIII}$  transformation occurs. No such slope change is evident. Is this curve related to the  $\text{Cd-Sb}$  eutectic temperature, or does it belong to some other phase, which although stable at 50 kbar,  $350^\circ\text{C}$ , decomposes at 50 kbar and lower temperatures to a mixture of  $\text{Cd}$  and  $\text{Sb}$ ? BELASH and PONYATOVSKII<sup>15</sup> noted that four weak diffraction lines could not be indexed as either pure  $\text{Cd}$  or pure  $\text{Sb}$ , and they attributed them to minor contaminations. It is possible that these four diffraction lines have a greater significance. *In situ* X-ray diffraction experiments at 60 kbar,  $300^\circ\text{C}$  are needed.

Does this decomposition of  $\text{CdSb}$  have a parallel for the present  $\text{CdAs}$  and  $\text{ZnAs}$  phases? If what was previously thought to be the melting curve of  $\text{CdAs}_2\text{II}$  is the melting curve of  $\text{CdAs}$ , then the parallel is clear. Above  $\sim 45$  kbar the melting curve of  $\text{CdAs}$  is already falling, as for  $\text{CdSb}$  at 1 bar. Will  $\text{CdAs}$  decompose further at still higher pressures,

Table III. Experiments made on pure  $\text{CdAs}_2$  to check the relationship between  $\text{CdAs}$  and phase D.

| Starting substance   | Treatment                                                                                                                                                                                                                                                                                                 | Product                      |
|----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| Pure $\text{CdAs}_2$ | 40 kbar, $650^\circ\text{C}$ for $\frac{1}{2}$ hour – cool slowly at 40 kbar to $\sim 20^\circ\text{C}$ – hold for $\frac{1}{2}$ hour – heat slowly to $500^\circ\text{C}$ at 40 kbar – hold for 1 hour – quench to ambient.                                                                              | Phase D + As                 |
| Pure $\text{CdAs}_2$ | 40 kbar, $500^\circ\text{C}$ for $\frac{1}{4}$ hour – heat to $650^\circ\text{C}$ at 40 kbar, and hold for 1 minute – quench to ambient.                                                                                                                                                                  | Phase D + As                 |
| Pure $\text{CdAs}_2$ | 40 kbar, $500^\circ\text{C}$ for $\frac{1}{4}$ hour – heat to $650^\circ\text{C}$ at 40 kbar, and hold for 1 minute – slow cool at 40 kbar to $\sim 20^\circ\text{C}$ – hold for $\frac{1}{2}$ hour – heat slowly to $500^\circ\text{C}$ at 40 kbar, and hold for $\frac{3}{4}$ hour – quench to ambient. | $\text{CdAs}$ (phase C) + As |