

were read from previously determined calibration curves<sup>6</sup>, and are believed to be correct to within  $\pm 5^\circ\text{C}$  and  $\pm 2$  kbar respectively. The pressure and temperature calibration curves were repeated at intervals during the present study, and were always within the above mentioned limits.

The samples were contained in BN with no evidence of reaction. Niobium capsules similar to those used by CLARK and PISTORIUS<sup>5</sup> yielded identical results to those obtained with BN.

In all experiments pressure was first increased and maintained until constant, when the temperature was increased slowly to the desired value. Unless otherwise mentioned, the pressure temperature conditions were held constant for 10 minutes, after which time temperature and pressure were quenched to ambient. Longer periods at high pressure and temperature did not influence results. The products were examined using a Huber-Guinier camera (film and counter methods), and monochromatized  $\text{CuK}\alpha_1$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation.

### Results

$\text{ZnAs}_2$  and  $\text{CdAs}_2$  yielded quenchable phases above  $\sim 30$  kbar,  $\sim 400^\circ\text{C}$ . Surprisingly, however, the X-ray investigations showed that a substantial amount of free As was present in the reaction products. These results indicated that unexpected decomposition reactions take place at high pressure, to assemblages containing a new high pressure phase with unknown composition and free As. The previous<sup>5</sup> notation  $\text{ZnAs}_2\text{II}$  and  $\text{CdAs}_2\text{II}$  used for these high pressure phases is therefore in error. However, nothing in the previous experiments<sup>5</sup> suggested a change in composition, and they were not designed to observe such a change. Efforts to

determine the composition of the high pressure phases resulted in experiments being made on mixtures with compositions differing from that of  $\text{CdAs}_2$  and  $\text{ZnAs}_2$ . Tables I and II summarize these experiments. All results on the phase diagrams in Figs. 1 and 6 are from experiments on  $\text{ZnAs}_2$  and  $\text{CdAs}_2$ , respectively.

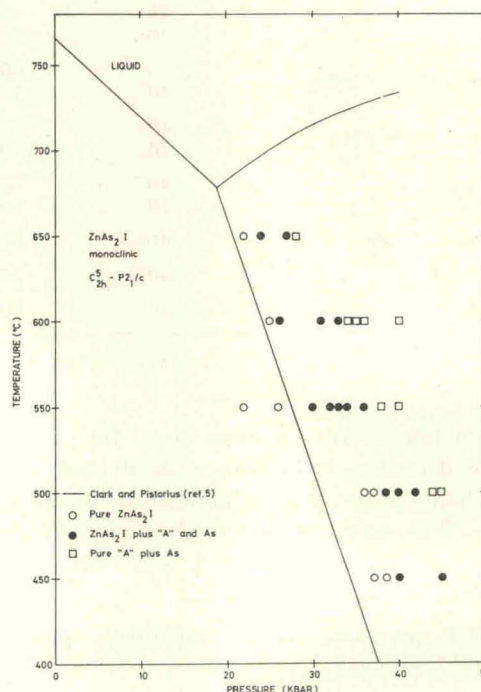


Fig. 1. Phase diagram of  $\text{ZnAs}_2$ , including previously determined phase boundaries<sup>5</sup> and present results.

Table I. Characteristic results on the phases obtained from high pressures and temperatures at various compositions in the  $\text{Zn}_3\text{As}_2$ -As system.

Composition of starting mixtures	P [kbar]	T [ $^\circ\text{C}$ ]	Phases identifiable using X-ray diffraction				
			$\text{ZnAs}_2\text{I}$	A	B	As	$\text{Zn}_3\text{As}_2$
Pure $\text{ZnAs}_2$	$< 30$	550	×				
	$38 > P > 30$	550	×	×		×	×
	$> 38$	550		×		×	
	40	1200			×	×	
$\text{Zn}_3\text{As}_2 + \text{As} \rightarrow \text{ZnAs}_{0.8}$	40	1000		×			×
$\text{Zn}_3\text{As}_2 + \text{As} \rightarrow \text{ZnAs}_{1.11}$	40	1000		×		×	×
$\text{Zn}_3\text{As}_2 + \text{As} \rightarrow \text{ZnAs}$	40	800		×		×	×
	40	1200			×	×	×
Pure $\text{Zn}_3\text{As}_2$	40	600					×
	40	1200					×
$\text{Zn} + \text{As} \rightarrow \text{ZnAs}$	40	1000		×		×	×

× = Strongly present. × × = Weakly present. × × × = Very weakly present.



Table II. Characteristic results on the phases obtained from high pressures and temperatures at various compositions in the  $\text{Cd}_3\text{As}_2$ -As system.

Composition of starting mixtures	P [kbar]	T [°C]	Phases identifiable using X-ray diffraction				
			$\text{CdAs}_2\text{I}$	C	D	As	$\text{Cd}_3\text{As}_2$ glass
Pure $\text{CdAs}_2$	<18	415	×				
	32 > P > 18	415	×	×	×		
	42 > P > 32	415	×	×		×	
	P > 42	415		×		×	
	40	> 650			×	×	
	10	800					×
$\text{Cd}_3\text{As}_2 + \text{As} \rightarrow \text{CdAs}_2$	40	1200				×	×
	40	600		×	×	×	×
$\text{Cd}_3\text{As}_2 + \text{As} \rightarrow \text{CdAs}$	40	> 700			×	×	
	40	< 850				×	×
$\text{Cd} + \text{As} \rightarrow \text{CdAs}_2$	40	1000			×	×	×
	40	600		×	×	×	×
$\text{Cd} + \text{As} \rightarrow \text{CdAs}$	40	800		×	×	×	×
	40	800			×	×	×
Pure $\text{Cd}_3\text{As}_2$	40	750					×
Pure As	40	600				×	

× = Strongly present. × × = Weakly present. × × × = Very weakly present.

If the temperature is raised above the previously proposed melting temperatures at 40 kbar, further quenchable phases are produced for both  $\text{ZnAs}_2$  and  $\text{CdAs}_2$ . The presence of free As also indicated a similar decomposition process. For simplicity the following notation will be used;

- i) High pressure, lower temperature phase for  $\text{ZnAs}_2$  - Phase A,
- ii) High pressure, higher temperature phase for  $\text{ZnAs}_2$  - Phase B,
- iii) High pressure, lower temperature phase for  $\text{CdAs}_2$  - Phase C,
- iv) High pressure, higher temperature phase for  $\text{CdAs}_2$  - Phase D.

The present paper will describe the influence of pressure and temperature on the decomposition reactions, efforts to determine the exact composition of Phases A and C, resistance measurements, the relationships between the phases found and the relationship to the previous work<sup>5</sup>. In another paper<sup>7</sup> the crystallographic aspects of the high pressure phases will be discussed.

#### $\text{Zn}_3\text{As}_2$ -As system

Table I presents characteristic results within this system. Fig. 1 shows the phase diagram of

$\text{ZnAs}_2$ . All work presented on this diagram had  $\text{ZnAs}_2$  as a starting material and earlier results are also included.

At each of five isotherms runs were made, which yielded similar results. At lower pressures only  $\text{ZnAs}_2\text{I}$  is found. This is followed by a region ~4-8 kbar wide, depending on the temperature, where a mixture of  $\text{ZnAs}_2\text{I}$ , As and phase A are found. Finally beyond this region only As and phase A are found. The present results produce a boundary for the decomposition of  $\text{ZnAs}_2\text{I}$  into phase A and As, which is slightly higher than the previously proposed<sup>5</sup>  $\text{ZnAs}_2\text{I/II}$  phase boundary. This is not surprising in view of the large uncertainties involved in the previous<sup>5</sup> tentative determination and it is certain that what was thought to be the  $\text{ZnAs}_2\text{I/II}$  phase boundary is the present decomposition boundary.

A run at 10 kbar, 600 °C was made, where the pressure temperature conditions were maintained for 1 hour. On quenching, only  $\text{ZnAs}_2\text{I}$  was found to be present, thus proving that the decomposition process is not time dependant.

The resistance of a sliver of  $\text{ZnAs}_2$  was monitored with increasing pressure along the 550 °C and 600 °C isotherms. In both cases a sharp discontinuous drop of ~70% in the resistance was found at 32 kbar and 25 kbar respectively, in excellent