

were read from previously determined calibration curves⁶, and are believed to be correct to within $\pm 5^\circ\text{C}$ and $\pm 2\text{ kbar}$ 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 PISTORIUS⁵ 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

ZnAs_2 and CdAs_2 yielded quenchable phases above $\sim 30\text{ kbar}$, $\sim 400^\circ\text{C}$. 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 previous⁵ notation ZnAs_2II and CdAs_2II used for these high pressure phases is therefore in error. However, nothing in the previous experiments⁵ 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 CdAs_2 and ZnAs_2 . Tables I and II summarize these experiments. All results on the phase diagrams in Figs. 1 and 6 are from experiments on ZnAs_2 and CdAs_2 , respectively.

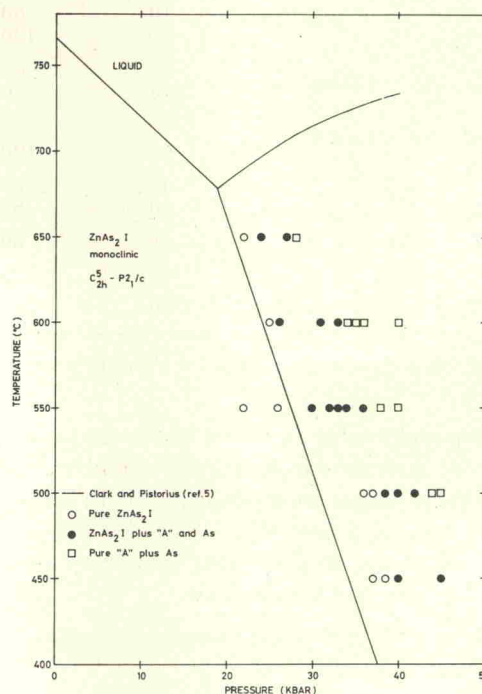


Fig. 1. Phase diagram of ZnAs_2 , including previously determined phase boundaries⁵ and present results.

Table I. Characteristic results on the phases obtained from high pressures and temperatures at various compositions in the Zn_3As_2 -As system.

Composition of starting mixtures	P [kbar]	T [$^\circ\text{C}$]	Phases identifiable using X-ray diffraction				
			ZnAs_2I	A	B	As	Zn_3As_2
Pure 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 Zn_3As_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 Cd_3As_2 -As system.

Composition of starting mixtures	P [kbar]	T [°C]	Phases identifiable using X-ray diffraction				
			CdAs_2I	C	D	As	Cd_3As_2 glass
Pure 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 Cd_3As_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 ZnAs_2 and 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 ZnAs_2 - Phase A,
- ii) High pressure, higher temperature phase for ZnAs_2 - Phase B,
- iii) High pressure, lower temperature phase for CdAs_2 - Phase C,
- iv) High pressure, higher temperature phase for 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 work⁵. In another paper⁷ the crystallographic aspects of the high pressure phases will be discussed.

Zn_3As_2 -As system

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

ZnAs_2 . All work presented on this diagram had 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 ZnAs_2I is found. This is followed by a region ~4-8 kbar wide, depending on the temperature, where a mixture of ZnAs_2I , 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 ZnAs_2I into phase A and As, which is slightly higher than the previously proposed⁵ $\text{ZnAs}_2\text{I/II}$ phase boundary. This is not surprising in view of the large uncertainties involved in the previous⁵ 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 ZnAs_2I was found to be present, thus proving that the decomposition process is not time dependant.

The resistance of a sliver of 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