were read from previously determined calibration curves⁶, and are believed to be correct to within ± 5 °C and ± 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 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 CuK_{a1} $(\lambda = 1,5405 \text{ Å})$ radiation.

Results

ZnAs₂ and CdAs₂ yielded quenchable phases above ~30 kbar, ~400 °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 ZnAs₂II and CdAs₂II 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 ZnAs₂, 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 [°C] | | Phases identifiable using X-ray diffraction | | | | | |
|---|-----------------|------|---|-----------------|---|------------------------|------------------------|--|
| or starting mixtures | | | Ziniszi | | D | 110 | 21131132 | |
| Pure ZnAs ₂ | <30 | 550 | × | | | | | |
| | 38 > P > 30 | 550 | × | $\times \times$ | | $\times \times$ | | |
| | > 38 | 550 | | × | | × | | |
| | 40 | 1200 | | | × | × | | |
| $\rm Zn_3As_2 + As \rightarrow ZnAs_{0,8}$ | 40 | 1000 | | × | | | $\times \times \times$ | |
| $\rm Zn_3As_2 + As \rightarrow ZnAs_{1,11}$ | 40 | 1000 | | × | | $\times \times \times$ | | |
| $\rm Zn_3As_2 + As \rightarrow ZnAs$ | 40 | 800 | | × | | $\times \times \times$ | $\times \times \times$ | |
| | 40 | 1200 | | | × | $\times \times \times$ | $\times \times \times$ | |
| Pure Zn ₃ As ₂ | 40 | 600 | | | | | × | |
| | 40 | 1200 | | | | | × | |
| $Zn + As \rightarrow ZnAs$ | 40 | 1000 | | × | | $\times \times \times$ | $\times \times \times$ | |
| $\operatorname{Zn} + \operatorname{As} \to \operatorname{ZnAs}$ | 40 40 | 1000 | | × | | $\times \times \times$ | ××× | |

 \times = Strongly present. $\times \times$ = Weakly present. $\times \times \times$ = Very weakly present.

| Composition of starting mixtures | P [kbar] | T [°C] | Pha CdAs ₂ I | ases ident C | tifiable us D | ing X-ra As | ay diffracti Cd ₃ As ₂ | on glass |
|--|---|--|----------------------------|-------------------|------------------|----------------|---|-------------|
| Pure CdAs ₂ | $\begin{array}{c} <\!18\\ 32\!>\!P\!>\!18\\ 42\!>\!P\!>\!32\\ P\!>\!42\\ 40\\ 10\\ 40\end{array}$ | $\begin{array}{r} 415 \\ 415 \\ 415 \\ 415 \\ 5650 \\ 800 \\ 1200 \end{array}$ | ×××× | × × × × × × | × | × × × × × × | × | × |
| $\mathrm{Cd}_3\mathrm{As}_2 + \mathrm{As} \rightarrow \mathrm{CdAs}_2$ | 40 40 | | | ××× | × | ×× | × | |
| $\mathrm{Cd}_3\mathrm{As}_2 + \mathrm{As} \to \mathrm{CdAs}$ | 40 40 | $<\!\!850\ 1000$ | | | × | × ×× | ××× | |
| $\mathrm{Cd} + \mathrm{As} \to \mathrm{CdAs}_2$ | 40 40 | 600 800 | | ××× | × | ×× | × | |
| $Cd + As \rightarrow CdAs$ | 40 | 800 | | | ××× | × | × | |
| Pure Cd ₃ As ₂ | 40 | 750 | | | | | × | |
| Pure As | . 40 | 600 | | | | × | | |

Table II. Characteristic results on the phases obtained from high pressures and temperatures at various compositions in the Cd₃As₂-As system.

 $\times =$ Strongly present. $\times \times =$ Weakly present. $\times \times \times =$ Very weakly present.

If the temperature is raised above the previously proposed melting temperatures at 40 kbar, further quenchable phases are produced for both ZnAs₂ and CdAs₂. 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 ZnAs₂ – Phase B,
- iii) High pressure, lower temperature phase for CdAs₂ Phase C,
- iv) High pressure, higher temperature phase for CdAs₂ 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.

Zn3As2-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 ZnAs₂I is found. This is followed by a region $\sim 4-$ 8 kbar wide, depending on the temperature, where a mixture of ZnAs₂I, 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 ZnAs₂I into phase A and As, which is slightly higher than the previously proposed⁵ ZnAs₂I/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 ZnAs₂I/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 dependent.

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

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