

High Pressure Reactions in the Systems Zn_3As_2 -As and Cd_3As_2 -As

J. B. CLARK* and KLAUS-JÜRGEN RANGE

Institut für Anorganische Chemie der Universität München

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ZnAs_2 and CdAs_2 decompose at high pressure and temperature. The determined decomposition boundaries are presented. From synthesis experiments in the systems Cd_3As_2 -As and Zn_3As_2 -As, the decomposition products were found to be mixtures of $\text{CdAs} + \text{As}$ and $\text{ZnAs} + \text{As}$. The high pressure phases CdAs and ZnAs are orthorhombic, space group $D_{2h}^{15} - \text{Pbca}$, with $a_0 = 5.993 \text{ \AA}$, $b_0 = 7.819 \text{ \AA}$, $c_0 = 8.010 \text{ \AA}$ and $a_0 = 5.679 \text{ \AA}$, $b_0 = 7.277 \text{ \AA}$, $c_0 = 7.559 \text{ \AA}$, respectively. Further phases are recovered from the high temperature region at high pressure.

Introduction

ZnAs_2^1 and $\text{CdAs}_2^{2,3}$ are normal tetrahedral compounds⁴ with relatively open structures. They are therefore expected to undergo solid-solid phase transitions to denser phases at high pressures. CLARK and PISTORIUS⁵ studied stable and metastable equilibria near the melting curves of ZnAs_2 and CdAs_2 to ~ 45 kbar by means of high pressure differential thermal analysis (D.T.A.). The melting curves of the stable atmospheric pressure phases fall with pressure to supposed triple points at ~ 20 kbar. The high pressure region was thought to contain the more dense phases ZnAs_2II and CdAs_2II , and consequently D.T.A. signals obtained in this region were ascribed to the melting of ZnAs_2II and CdAs_2II . The melting curve of ZnAs_2II rises with increasing pressure, while that of CdAs_2II , after initially rising with increasing pressure, passes through a maximum, and then falls with pressure. Certain heating patterns gave rise to additional D.T.A. signals which were ascribed to neighbouring

eutectics *viz.*, Cd_3As_2 - CdAs_2 , CdAs_2 -As and ZnAs_2 -As.

The high pressure solid-solid transformations lay beyond the range of the volumetric measurements made in the previous study⁵. However, the approximate location of the high pressure transformations was obtained using resistance and D.T.A. at constant temperature⁵. The unusually high uncertainty (~ 4 kbar) made an accurate determination of this boundary using other techniques important. The high pressure transformations were expected to become sluggish at lower temperatures.

Quenching experiments were therefore made to clarify the nature of the high pressure reaction products in the systems Zn_3As_2 -As and Cd_3As_2 -As.

Experimental

CdAs_2 and ZnAs_2 were prepared by direct synthesis of stoichiometric quantities of the elements (Merck z.A.), in evacuated quartz ampoules which were flushed with Argon prior to evacuation. The ampoules were heated to 600°C for 40 hours, cooled slowly, the products reground finely and heated at 600°C for a further 100 hours. The resulting materials were confirmed to be single phase by X-ray diffraction and the very sharp diffraction lines indicated that the materials were well crystallized. Other synthesis temperatures were tried, but the products were poorly crystallized or were not single phase. Zn_3As_2 and Cd_3As_2 were synthesized in a similar manner at 650°C .

Pressure was generated in a belt device. The complete experimental procedure has been described previously⁶. In all cases temperature and pressure

* Permanent address: National Physical Research Laboratory, South African Council for Scientific and Industrial Research, P. O. Box 395, Pretoria 0001, South Africa.

Requests for reprints should be sent to Dr. J. B. CLARK, National Physical Research Laboratory, South African Council for Scientific and Industrial Research, P. O. Box 395, Pretoria 0001, South Africa, or to: Prof. Dr. KLAUS-JÜRGEN RANGE, Institut für Chemie der Universität Regensburg, D-8400 Regensburg, Universitätsstraße 31.

were read from previously determined calibration curves⁶, and are believed to be correct to within $\pm 5^\circ\text{C}$ 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 $\text{CuK}\alpha_1$ ($\lambda = 1,5405 \text{ \AA}$) radiation.

Results

ZnAs_2 and CdAs_2 yielded quenchable phases above ~ 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 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.

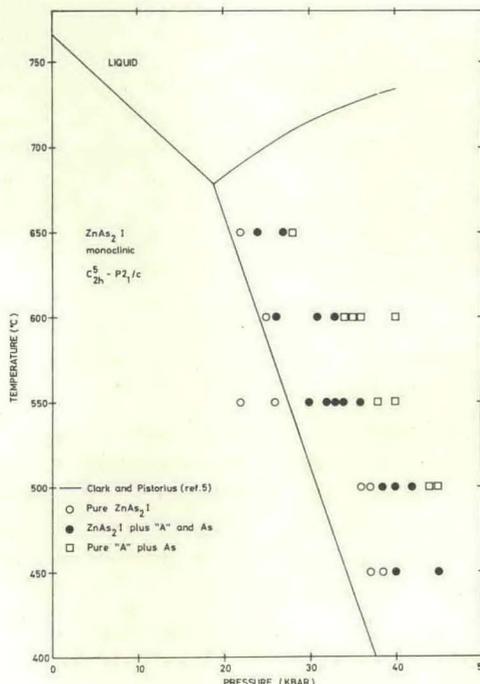


Fig. 1. Phase diagram of ZnAs_2 , including previously determined phase boundaries⁵ and present results.

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 | | | | | | × |
| $Cd_3As_2 + As \rightarrow CdAs_2$ | 40 | 600 | | × × × | | | × | |
| | 40 | > 700 | | | × | | × | |
| $Cd_3As_2 + As \rightarrow CdAs$ | 40 | < 850 | | | | | × | |
| | 40 | 1000 | | | × | | × × | × × |
| $Cd + As \rightarrow CdAs_2$ | 40 | 600 | | × × × | | | × | |
| | 40 | 800 | | | × | | × | |
| $Cd + As \rightarrow CdAs$ | 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 $ZnAs_2I/II$ 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 $ZnAs_2I/II$ 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

agreement with the results from the quenching experiments.

Attempts to determine the exact composition of phase A were made, by subjecting mixtures of Zn_3As_2 and As in varying compositions to 40 kbar and 800–1000 °C for 1 hour. The temperature was first lowered slowly to ~600 °C at 40 kbar, held for a further 5 minutes, before pressure and temperature were quenched to ambient. The results are summarized in Table I, and shown schematically in relation to the composition-temperature phase diagram⁸ in Fig. 2. The composition ZnAs yielded

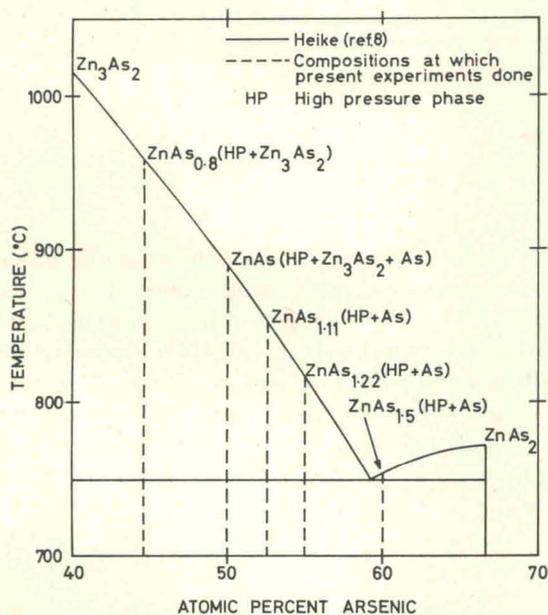


Fig. 2. Efforts to determine the composition of phase A, shown in relation to a portion of the composition-temperature diagram of Zn-As.

the bulk of the material as phase A, with very faint traces of unreacted Zn_3As_2 and As present. Fig. 3 shows X-ray traces on the run products with compositions $ZnAs_{0.8}$, ZnAs and $ZnAs_{1.22}$, clearly indicating the unchanged high pressure phase, with excesses of Zn_3As_2 and As present in the traces on $ZnAs_{0.8}$ and $ZnAs_{1.22}$ respectively.

ALEXANDER and KLUG's⁹ technique for quantitative analysis indicated within experimental uncertainty that ZnAs was the correct composition for phase A. Further confirmation was obtained by subjecting a 1:1 mixture of Zn and As to 40 kbar and 1000 °C for 1 hour.

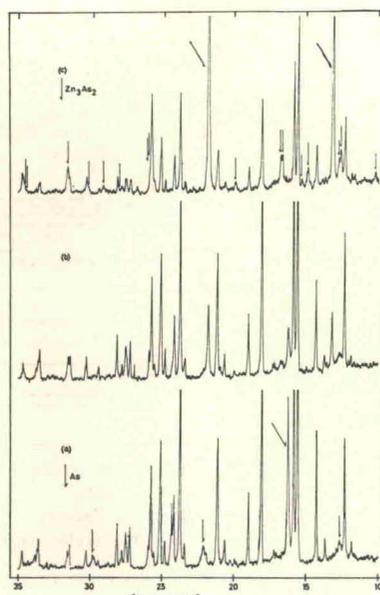


Fig. 3. X-ray diffraction traces of products from high pressure experiments to determine the composition of phase A.

- (a) Composition $ZnAs_{1.22}$ showing presence of excess As.
- (b) Composition ZnAs.
- (c) Composition $ZnAs_{0.8}$ showing presence of excess Zn_3As_2 .

The diffraction pattern obtained for phase A (ZnAs) was indexed using the method of de WOLFF¹⁰, and yielded an orthorhombic cell with $a_0 = 5.679 \text{ \AA}$, $b_0 = 7.277 \text{ \AA}$ and $c_0 = 7.559 \text{ \AA}$. Systematic absences showed that the space group is Pbc_a. Details of the crystallographic work will be published⁷.

On subjecting $ZnAs_2$, and mixtures of Zn_3As_2 and As having the ZnAs composition to 40 kbar, 1200 °C, a further quenchable phase, B, was found. Phase B yielded a diffraction pattern very rich in diffraction peaks. Strikingly once phase B was created at 40 kbar, 1200 °C for 1 hour, it did not retransform into phase A, even after tempering it at 40 kbar, 800 °C for 1 hour.

The products of various high pressure experiments were tempered in sealed quartz capillary tubes, at atmospheric pressure and a variety of temperatures for ~17 hours. Below 200 °C no change was visible, while between 200–350 °C some retransformation into the atmospheric phases occurred. A temperature of 350 °C was sufficient to

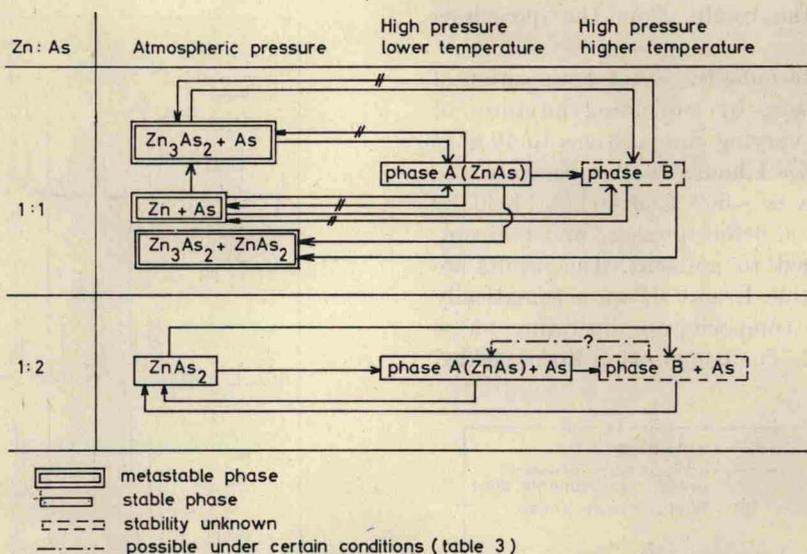


Fig. 4. Stability relationships between phases obtained from high pressures and high temperatures in the Zn₃As₂-As system.

produce a total change from the high pressure forms into the stable atmospheric pressure phases.

A schematic representation of present results at high pressure, including the relevant tempering results at atmospheric pressure, is presented in Fig. 4. This figure shows the relationships between the various phases obtained from mixtures of Zn₃As₂ and As in the ZnAs composition, and ZnAs₂.

Zn₃As₂ produced no quenchable phases, in agreement with earlier results^{11,12}, where quenching to 110 °K was necessary to retain high pressure phases for Cd₃As₂ and Zn₃As₂. Pure As also did not yield any quenchable phases.

All attempts to obtain single crystals of phases A and B failed. A variety of cooling treatments, fluxes of ZnI₂ and As, all yielded well compacted fine powders.

Cd₃As₂-As system

Table II presents characteristic results within the Cd₃As₂-As system. Fig. 5 shows the phase diagram of CdAs₂. Only work done on pure CdAs₂ is presented in this diagram together with previous results.

Experiments done along two isotherms at 415 °C and 515 °C yielded an interesting feature not found on the ZnAs₂ isotherms. At lower pressures only CdAs₂I exists. This is followed by a region ~10 kbar wide, where, although CdAs₂I is predominant, very

faint traces of phase C can be seen in the diffraction patterns, without any visible trace of free As. Substantially longer exposure times confirmed this result. It is possible that free As is present, but badly crystallized and in such small quantities that it is not detectable using X-ray diffraction. An equivalent zone was never found for ZnAs₂. Following this region was a region ~10 kbar wide, where

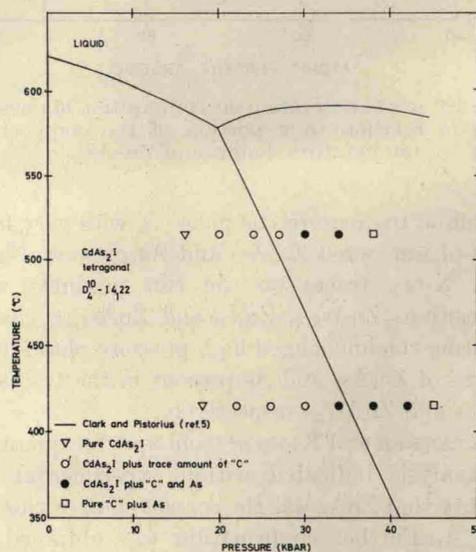


Fig. 5. Phase diagram of CdAs₂, including previously determined phase boundaries⁵ and present results.

CdAs_2I , phase C and As coexist. Finally at still higher pressures only phase C and As are found.

Resistance measurements along the 415°C isotherm yielded a break in the curve of resistance versus pressure at 33 kbar. This is the boundary between the region where CdAs_2I is predominant with traces of phase C present, but no As, and the region where CdAs_2I , phase C and As coexist. This point on both isotherms is in good agreement with the previously proposed⁵ $\text{CdAs}_2\text{I/II}$ phase boundary. As in the case of 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 CdAs_2 as was previously used⁵, was made, where the 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 Cd_3As_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 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 analysis⁹ 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 ZnAs_2 . The tempering time was ~ 17 hours and 300°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 WOLFF¹⁰, 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 Pbc. Details of the crystallographic work will be published⁷.

In an attempt to understand the relative stabilities phases C and D and therefore also phases A and B, the following experiments were made. CdAs_2 was held at 10 kbar, 900°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 pressure¹³. This suggests that phases D and B are the

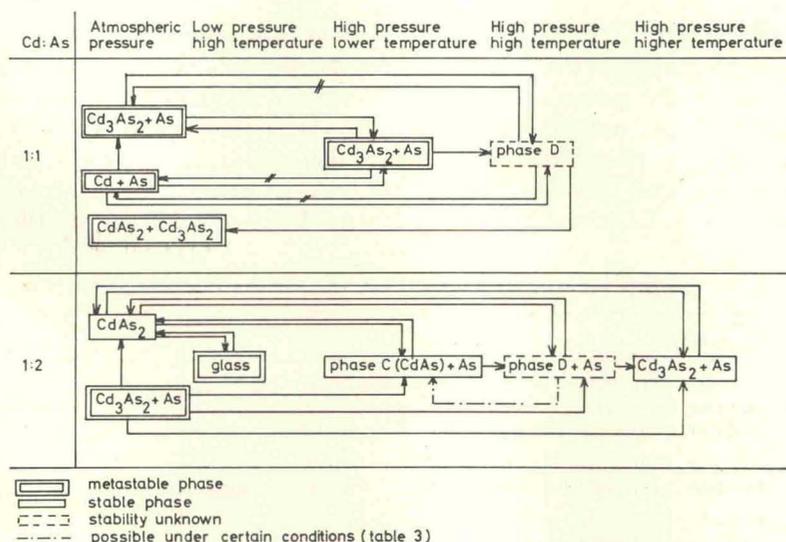


Fig. 6. Stability relationships between phases obtained from high pressures and high temperatures in the Cd_3As_2 -As system.

products of the high pressure, high temperature region only. In the previous study⁵, an extra set of signals obtained in the high pressure region, were ascribed to the CdAs₂II-As eutectic. From the present results it is known that CdAs₂II does not exist. It is therefore tempting to assume that these signals belong to the 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. signals⁵. 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 ~25 °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 previously⁵ thought to be the melting curves of CdAs₂II and ZnAs₂II are probably the melting curves of CdAs and ZnAs. The phases B and D are thought to be metastable, and probably involve some process in the liquids of CdAs and ZnAs.

The phases ZnAs and CdAs are isostructural⁷ with ZnSb and CdSb¹⁴. A recent paper on the phase diagram of CdSb¹⁵ indicated a falling melting curve for CdSb, followed by a region above ~35 kbar, where CdSb decomposes into Cd and Sb. Certain questions arise from this paper¹⁶. Above ~35 kbar, the rising portion of the melting curve, is attributed to the Cd-Sb eutectic. An extrapolation of this curve to 1 bar, yields ~30-50 °C for the metastable eutectic temperature. However, an estimate of the metastable eutectic temperature from the composition-temperature phase diagram, yields a value of ~150 °C. Although these values come from long extrapolations, the lack of agreement is noticeable. Furthermore, the SbII/III transformation causes a sharp break in the melting curve of Sb. Correspondingly there should be a slope change in the Cd-Sb eutectic temperature at ~65 kbar where the Cd-SbII to Cd-SbIII transformation occurs. No such slope change is evident. Is this curve related to the Cd-Sb eutectic temperature, or does it belong to some other phase, which although stable at 50 kbar, 350 °C, decomposes at 50 kbar and lower temperatures to a mixture of Cd and Sb? BELASH and PONYATOVSKII¹⁵ noted that four weak diffraction lines could not be indexed as either pure Cd or pure 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 °C are needed.

Does this decomposition of CdSb have a parallel for the present CdAs and ZnAs phases? If what was previously thought to be the melting curve of CdAs₂II is the melting curve of CdAs, then the parallel is clear. Above ~45 kbar the melting curve of CdAs is already falling, as for CdSb at 1 bar. Will CdAs decompose further at still higher pressures,

Table III. Experiments made on pure CdAs₂ to check the relationship between CdAs and phase D.

| Starting substance | Treatment | Product |
|------------------------|---|---------------------|
| Pure CdAs ₂ | 40 kbar, 650 °C for 1/2 hour - cool slowly at 40 kbar to ~20 °C - hold for 1/2 hour - heat slowly to 500 °C at 40 kbar - hold for 1 hour - quench to ambient. | Phase D + As |
| Pure CdAs ₂ | 40 kbar, 500 °C for 1/4 hour - heat to 650 °C at 40 kbar, and hold for 1 minute - quench to ambient. | Phase D + As |
| Pure CdAs ₂ | 40 kbar, 500 °C for 1/4 hour - heat to 650 °C at 40 kbar, and hold for 1 minute - slow cool at 40 kbar to ~20 °C - hold for 1/2 hour - heat slowly to 500 °C at 40 kbar, and hold for 3/4 hour - quench to ambient. | CdAs (phase C) + As |

and if so, into what? From the volume relationships listed in Table IV it becomes apparent that the further decomposition of CdAs into Cd and As is indeed possible and is more favourable than the other probable decomposition reaction of 3 CdAs \rightarrow Cd₃As₂III + As. At this point it is also relevant to note that, although volume relationships indicate possible decomposition reactions at high pressures, they are only indications. For example from Table IV it is apparent that the CdAs₂ \rightarrow Cd + 2 As decomposition reaction is favourable. However, it does not take place as is shown by the present results.

Table IV. Volume relationships of probable high pressure reactions.

| High pressure reactions | $\Delta V/V_0$ |
|---|----------------|
| CdAs ₂ \rightarrow CdAs + As | - 7,2% |
| CdAs \rightarrow Cd + As | - 8,1% |
| 3 CdAs \rightarrow Cd ₃ As ₂ III + As | - 1,8% |
| CdAs ₂ \rightarrow Cd + 2 As | - 12,4% |
| ZnAs ₂ \rightarrow ZnAs + As | - 13,2% |
| ZnAs \rightarrow Zn + As | - 5,9% |
| 3 ZnAs \rightarrow Zn ₃ As ₂ III + As | - 3,0% |
| ZnAs ₂ \rightarrow Zn + 2 As | - 16,6% |

The volume relationships for ZnAs show the same tendencies, but the melting curve of ZnAs is still rising at 40 kbar. It is therefore possible that the melting curve of ZnAs will first pass through a maximum, and then at even higher pressure ZnAs might also decompose. This suggests that ZnAs might be stable over a longer pressure range than CdAs.

The composition temperature diagrams of Cd-As and Zn-As at high pressure can be expected to undergo many changes. Above \sim 20 kbar the compounds CdAs₂ and ZnAs₂ must disappear and

the compounds CdAs and ZnAs must appear. The Cd₃As₂-CdAs₂, CdAs₂-As, Zn₃As₂-ZnAs₂ and ZnAs₂-As eutectics also therefore no longer exist and are replaced by the Cd₃As₂-CdAs, CdAs-As, Zn₃As₂-ZnAs and ZnAs-As eutectics. However, if ZnAs and CdAs decompose at still higher pressures, then the composition-temperature diagrams change again and will only contain the compounds Cd₃As₂ and Zn₃As₂.

ZnAs was readily synthesized from mixtures of Zn₃As₂ and As at 40 kbar, 800-1000 °C. However, CdAs could not be synthesized from mixtures of Cd₃As₂ and As under the same pressure, temperature conditions. These problems are related to the shapes of the melting curves of CdAs and ZnAs. The melting curve of ZnAs rises with increasing pressure and this implies that the synthesis temperatures of 800-1000 °C used for ZnAs are only 50-250 °C above the melting temperature of ZnAs at 40 kbar. The maximum in the melting curve of CdAs forces the CdAs to melt at lower temperatures at 40 kbar than ZnAs. Thus at 800 °C, the lowest synthesis temperature used for ZnAs, we are already 200 °C above the melting temperature of CdAs. Phase D was found only 50 °C above the melting temperature of CdAs, and therefore ideally CdAs should be synthesized from Cd₃As₂ and As at \sim 450 °C at 40 kbar. However, at 40 kbar As and Cd₃As₂ melt at \sim 1000 °C and \sim 700 °C respectively, and so would not be molten. This would result in very long reaction time at 40 kbar, which presents problems as far as pressure application is concerned.

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