

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  $\rightarrow$  Cd<sub>3</sub>As<sub>2</sub>III + 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 CdAs<sub>2</sub>  $\rightarrow$  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 <sub>2</sub> $\rightarrow$ CdAs + As	— 7,2%
CdAs $\rightarrow$ Cd + As	— 8,1%
3 CdAs $\rightarrow$ Cd <sub>3</sub> As <sub>2</sub> III + As	— 1,8%
CdAs <sub>2</sub> $\rightarrow$ Cd + 2 As	— 12,4%
ZnAs <sub>2</sub> $\rightarrow$ ZnAs + As	— 13,2%
ZnAs $\rightarrow$ Zn + As	— 5,9%
3 ZnAs $\rightarrow$ Zn <sub>3</sub> As <sub>2</sub> III + As	— 3,0%
ZnAs <sub>2</sub> $\rightarrow$ 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 ~20 kbar the compounds CdAs<sub>2</sub> and ZnAs<sub>2</sub> must disappear and

the compounds CdAs and ZnAs must appear. The Cd<sub>3</sub>As<sub>2</sub>-CdAs<sub>2</sub>, CdAs<sub>2</sub>-As, Zn<sub>3</sub>As<sub>2</sub>-ZnAs<sub>2</sub> and ZnAs<sub>2</sub>-As eutectics also therefore no longer exist and are replaced by the Cd<sub>3</sub>As<sub>2</sub>-CdAs, CdAs-As, Zn<sub>3</sub>As<sub>2</sub>-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 Cd<sub>3</sub>As<sub>2</sub> and Zn<sub>3</sub>As<sub>2</sub>.

ZnAs was readily synthesized from mixtures of Zn<sub>3</sub>As<sub>2</sub> and As at 40 kbar, 800–1000 °C. However, CdAs could not be synthesized from mixtures of Cd<sub>3</sub>As<sub>2</sub> 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 Cd<sub>3</sub>As<sub>2</sub> and As at ~450 °C at 40 kbar. However, at 40 kbar As and Cd<sub>3</sub>As<sub>2</sub> melt at ~1000 °C and ~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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<sup>1</sup> M. E. FLEET, *Acta Crystallogr.* **B 30**, 122 [1974].

<sup>2</sup> J. HORN and K. LUKASZEWICZ, *Rocz. Chem.* **42**, 993 [1968].

<sup>3</sup> L. ČERVINKA and A. HRUBÝ, *Acta Crystallogr.* **B 26**, 457 [1970].

<sup>4</sup> E. PARTHÉ, in "Cristallochimie des Structures Tétraédriques", Gordon and Breach, New York 1972.

<sup>5</sup> J. B. CLARK and C. W. F. T. PISTORIUS, *High Temp.-High Press.* **5**, 319 [1973].

<sup>6</sup> K.-J. RANGE and R. LEEB, *Z. Naturforsch.*, to be published.

<sup>7</sup> J. B. CLARK and K.-J. RANGE, *Z. Naturforsch.*, to be published.

<sup>8</sup> W. HEIKE, *Z. Anorg. Allg. Chem.* **118**, 264 [1921].

<sup>9</sup> L. V. AZÁROFF and M. J. BUERGER, in "The Powder Method", pp. 200–208, McGraw-Hill, New York 1958.

<sup>10</sup> P. M. DE WOLFF, *Acta Crystallogr.* **10**, 590 [1957].

<sup>11</sup> H. KATZMAN, T. DONOHUE, and W. F. LIBBY, *Phys. Rev. Letters* **20**, 442 [1968].

<sup>12</sup> M. D. BANUS and M. C. LAVINE, *High Temp.-High Press.* **1**, 269 [1969].

<sup>13</sup> Y. A. UGAI, T. A. ZYUBINA, and K. B. ALENIKOVA, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **4**, 17 [1968].

<sup>14</sup> K. E. ALMIN, *Acta Chem. Scand.* **2**, 400 [1948].

<sup>15</sup> I. T. BELASH and E. G. PONYATOVSKII, *High Temp.-High Press.* **6**, 241 [1974].

<sup>16</sup> C. W. F. T. PISTORIUS, personal communication, 1975.