

# High Pressure Reactions in the Systems $\text{Zn}_3\text{As}_2$ -As and $\text{Cd}_3\text{As}_2$ -As

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$\text{ZnAs}_2$  and  $\text{CdAs}_2$  decompose at high pressure and temperature. The determined decomposition boundaries are presented. From synthesis experiments in the systems  $\text{Cd}_3\text{As}_2$ -As and  $\text{Zn}_3\text{As}_2$ -As, the decomposition products were found to be mixtures of  $\text{CdAs} + \text{As}$  and  $\text{ZnAs} + \text{As}$ . The high pressure phases  $\text{CdAs}$  and  $\text{ZnAs}$  are orthorhombic, space group  $\text{D}_{2h}^{15} - \text{Pbca}$ , 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

$\text{ZnAs}_2$ <sup>1</sup> and  $\text{CdAs}_2$ <sup>2,3</sup> are normal tetrahedral compounds<sup>4</sup> with relatively open structures. They are therefore expected to undergo solid-solid phase transitions to denser phases at high pressures. CLARK and PISTORIUS<sup>5</sup> studied stable and metastable equilibria near the melting curves of  $\text{ZnAs}_2$  and  $\text{CdAs}_2$  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  $\text{ZnAs}_2\text{II}$  and  $\text{CdAs}_2\text{II}$ , and consequently D.T.A. signals obtained in this region were ascribed to the melting of  $\text{ZnAs}_2\text{II}$  and  $\text{CdAs}_2\text{II}$ . The melting curve of  $\text{ZnAs}_2\text{II}$  rises with increasing pressure, while that of  $\text{CdAs}_2\text{II}$ , 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.*,  $\text{Cd}_3\text{As}_2$ - $\text{CdAs}_2$ ,  $\text{CdAs}_2$ -As and  $\text{ZnAs}_2$ -As.

The high pressure solid-solid transformations lay beyond the range of the volumetric measurements made in the previous study<sup>5</sup>. However, the approximate location of the high pressure transformations was obtained using resistance and D.T.A. at constant temperature<sup>5</sup>. 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  $\text{Zn}_3\text{As}_2$ -As and  $\text{Cd}_3\text{As}_2$ -As.

## Experimental

$\text{CdAs}_2$  and  $\text{ZnAs}_2$  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.  $\text{Zn}_3\text{As}_2$  and  $\text{Cd}_3\text{As}_2$  were synthesized in a similar manner at 650 °C.

Pressure was generated in a belt device. The complete experimental procedure has been described previously<sup>6</sup>. In all cases temperature and pressure

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