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 diagram[8] in Fig. 2. The composition ZnAs yielded

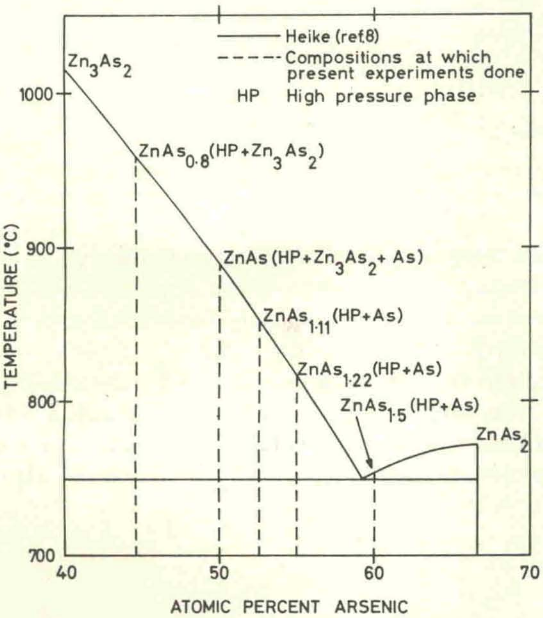

Fig. 2. Efforts to determine the composition of phase A, shown in relation to a portion of the composition temperature diagram of Zn–As.

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's[9] 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.

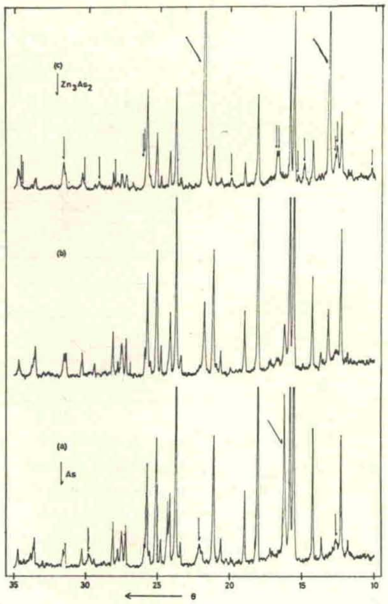

Fig. 3. X-ray diffraction traces of products from high pressure experiments to determine the composition of phase A.

(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 Wolff[10], and yielded an orthorhombic cell with $a_o = 5.679$ Å, $b_o = 7.277$ Å and $c_o = 7.559$ Å. Systematic absences showed that the space group is Pbca. Details of the crystallographic work will be published[7].

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

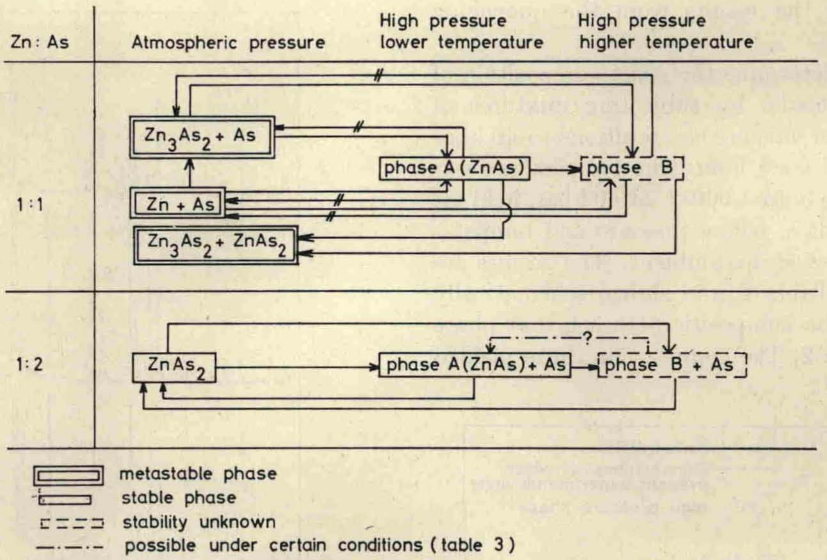

Fig. 4. Stability relationships between phases obtained from high pressures and high temperatures in the Zn_3As_2–As system.

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 Zn_3As_2 and As in the ZnAs composition, and $ZnAs_2$.

Zn_3As_2 produced no quenchable phases, in agreement with earlier results[11, 12], where quenching to 110 °K was necessary to retain high pressure phases for Cd_3As_2 and Zn_3As_2. 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 ZnI_2 and As, all yielded well compacted fine powders.

Cd_3As_2–As system

Table II presents characteristic results within the Cd_3As_2–As system. Fig. 5 shows the phase diagram of $CdAs_2$. Only work done on pure $CdAs_2$ 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 $ZnAs_2$ isotherms. At lower pressures only $CdAs_2I$ exists. This is followed by a region ~10 kbar wide, where, although $CdAs_2I$ 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 $ZnAs_2$. Following this region was a region ~10 kbar wide, where

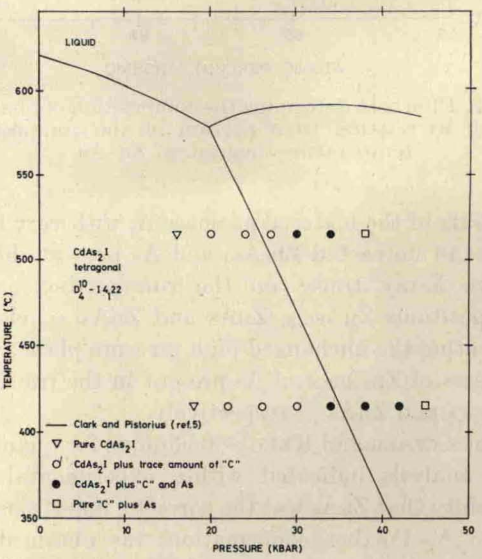

Fig. 5. Phase diagram of $CdAs_2$, including previously determined phase boundaries[5] and present results.