gradually diminishing in size. Repeating such preheating procedure reproduced this behavior. No such preheating was necessary above ~ 6 kbar and repeated DTA signals with somewhat gradually increasing size were obtained to the highest pressure attained. Such preheating was also found necessary in the other chalcogenides studied here with the exception of Ag_2S, and is, in our opinion, connected with the non-stiochiometric nature of these compounds. It is possible that the phase transition occurs only over a certain range of deviation from stoichiometric composition and that preheating treatment was necessary in order to introduce a certain amount of excess cation defects. The Ag–Se composition phase diagram is not as well established as those of Ag–S[6] or Ag–Te [23, 21]. The fragmentary diagram given by Hansen and Anderko[5] is based only on some early data and we do not know of any more recent data. The dependence of the transition temperature, mechanism and kinetics on excess Ag or Se in Ag_2Se is not known.

The phase diagram of Ag_2Se to 300°C and 40 kbar is shown in Fig. 3 and includes also the data of Banus[9] for comparison. The agreement with Banus's results is good to 20 kbar. Above 20 kbar Banus's results fall some 10°–15°C below our results. The initial slope, dT/dp, of 6·02°C/kbar is lower than the value 7·2°C/kbar reported by Roy *et al.*[7] as in the case of Ag_2S. The agreement with Banus's data below 20 kbar shows that our preheating treatment did not change the Ag_2Se sample drastically. The mode of preparation of our sample obtained from a commercial source is not known to us. Banus's sample was grown from the melt and had, thus, received a preheating treatment. Differences in behavior (resistance jump at the transition) for samples cooled from 700°–900°C as compared to samples cooled from temperature slightly above the transition were reported by Baer *et al.*[24, 9]. Banus[9] also reported that the hysteresis interval between the transition temperatures on heating and on cooling was 15°–25°C whereas in our experiments it did not exceed 3°C.

Silver telluride

The phase diagram of Ag_2Te to 40 kbars and 400°C is shown in Fig. 4. It also contains recent results of Banus and Finn[10] that appeared after our experimental work was completed. The phase designation has been kept in accord with Frueh[21] and is also consistent with the labelling in the case of Ag_2S [6]. The high-pressure phases recently discovered by Banus and Finn[10] had to be relabelled IV and V (instead of II and III, respectively, as originally labelled by Banus and Finn[10]).

In our experiments the preheating treatment was similar to that given in the case of Ag_2Se, and, similarly, was unnecessary above ~ 6 kbars. Ag_2Te used by Banus and Finn was grown from the melt, and therefore had also received a 'preheating treatment'. The good agreement between the results of Banus and Finn and our data on the III/II boundary demonstrates, again as in the case of Ag_2Se, that the preheating treatment produced essentially a sample of excess silver in the range of deviation from stoichiometry that exhibits the III/II transition. The composition phase diagram of the binary system Ag–Te [23] shows clearly that the III/II transition exists on the silver-rich side at 145° ± 3°C, whereas on the silver-deficient side complicated behavior due to coexistence of $Ag_{5-x}Te_3$, Ag_2Te and a γ-phase was reported by Kracek and Ksanda[25]. The prehating treatment that we used thus ensured equilibrium of Ag_2Te with excess Ag, as is also apparent from our 1 bar value of 147° ± 1°C. The latter value compares favorably with that of Kracek *et al.* [23] and also with the recent value of 148° ± 1°C of Banus and Finn[10] where a sample of known carrier concentration was used. Hysteresis between heating and cooling in our experiments did not exceed 4°C below ~ 6 kbar. Above ~ 6 kbars the transition on cool-

ing (II/III) took place some 20°C lower than on heating (III/II), yielding somewhat broader DTA signals. Banus and Finn[10] reported a triple point at 8 kbar, 200°C, the existence of which is, however, masked by the 10°–15°C scatter in their data on the f.c.c.-monoclinic boundary (II/III boundary in our notation). It can be inferred only from extrapolation of the III/IV or IV/V boundary. The possible slight break in the III/II transition line is not even obvious from our data, but the sudden increase in the hysteresis interval above 8 kbars may be of some indication. Above 30 kbars the DTA signal size was suddenly reduced to less than half of its previous size and the hysteresis interval decreased to about 12°C. Simultaneously, a small but definite upward break occurs on the V/II phase boundary, as is seen in Fig. 4, which is an indication of a new triple point and the appearance of a new high-pressure phase, Ag_2TeVI. The possible V/VI boundary is indicated in Fig. 4 by the dotted line. Unfortunately we did not have a sufficient amount of high purity Ag_2Te sample to perform volumetric work in order to detect the III/IV, IV/V and V/VI transitions by the piston-displacement method.

Cuprous sulfide

Phase behavior in the binary system copper–sulfur is more complex than in the silver chalcogenides discussed before. Djurle[26] studied phase relations in the Cu–S system by high temperature X-ray methods and found in samples prepared from the elements by sintering at temperatures of 320°C or 470°C the compounds Cu_2S, $Cu_{1.96}S$ and $Cu_{1.8}S$ (digenite). The three compounds undergo phase transitions[27]. A composition phase diagram of the binary system Cu–S was recently published by Rau[28] who argued in favor of the formula Cu_7S_4 rather than Cu_9S_5 ($Cu_{1.8}S$) for digenite. Earlier data by Buerger[29] are open to question due to the mode of sample preparation in air[26]. Djurle[26] showed that in the presence of excess copper, samples quenched from 400°C produced only Cu_2S and free copper. Our samples, enclosed in copper capsules and given a preheating treatment at 380°C were, therefore, in the Cu_2S composition. The course of the IV/III transformation [30] with pressure is shown in Fig. 5. The transition temperature increases with pressure from its zero pressure value of 103°C with an initial slope, dT/dp, of 0·5°C/kbar. At about 10 kbars new DTA signals were obtained around 240°C and the new transition line (Fig. 5) could be followed with ease, and without any necessity for preheating, to 40 kbars. At the same time, apart from some metastable extension beyond 10 kbars, the signals corresponding to the original IV/III transition disappeared. On releasing pressure this behavior is reversed and at around 8 kbars the upper transition disappeared and DTA signals corresponding to the lower IV/III transition were regained. The upper transition line varies only slightly with pressure and passes through a shallow maximum around 245°C and 21 kbar, the occurrence of which is probably connected with the disordered structure of the III phase (this will be discussed further). Serebrianaia[31] recently reported that $Cu_{1.96}S$ could be prepared by heating Cu_2S to 900°C. We therefore heated Cu_2S to ~850°C and after cooling we searched for the transition around 103°C with negative results. New, very sharp, DTA signals were, on the other hand, obtained around 220°–230° (see Fig. 6). This boundary is exactly parallel to the upper transition line in Fig. 5, but some ~10°C lower. We therefore think that the upper transition line in Fig. 5 corresponds to Cu_9S_5 (or Cu_7S_4) reversibly formed by a disproportionation reaction from Cu_2S. Both Cu_9S_5 samples formed in situ in the presence of Cu and Cu_2S are probably not very pure, and hence the 10°C difference in transition temperatures.

The temperature-hysteresis interval in the case of Cu_2S IV/III was varied and ranged between 1°–12°C. However, in the case of Cu_xS II/I it varied between 0°–2°C.

The Cu_2S III/II and II/I transitions were