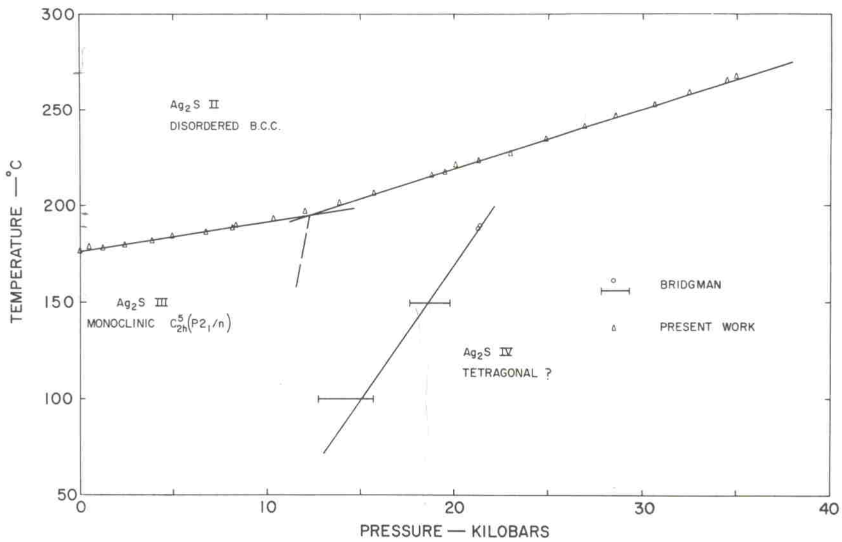

Fig. 2. Phase diagram of Ag_2S.

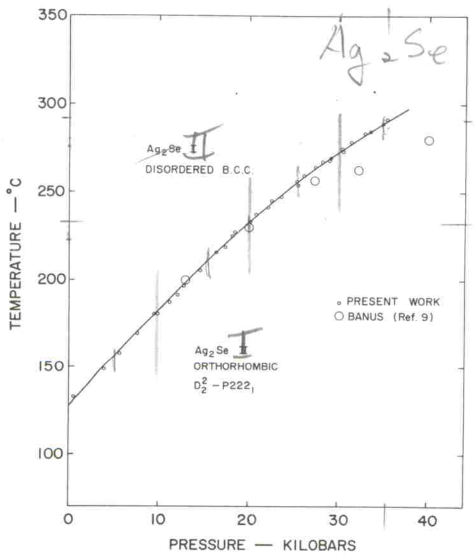

Fig. 3. Phase diagram of Ag_2Se to 300°C and 40 kbars (including the work of Banus).

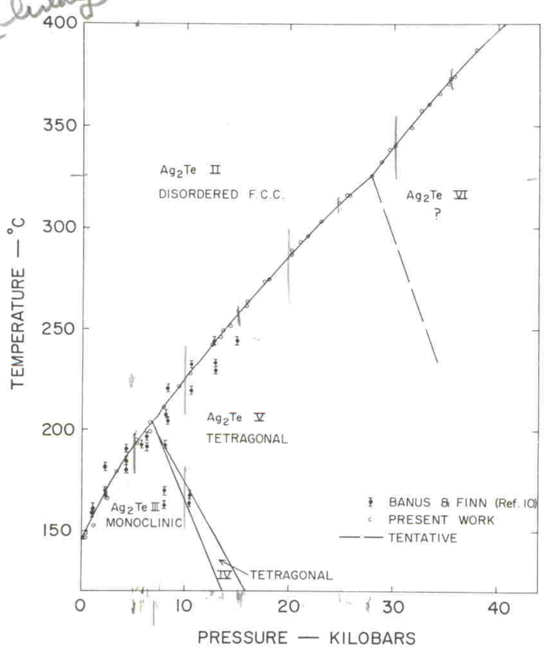

Fig. 4. Phase diagram to 400°C and 40 kbars of Ag_2Te (including the work by Banus and Finn).

of the II/III/IV triple point is the one at 12·3 kbar, 195°C. However, its location is not on the extrapolation of Bridgman's III/IV boundary. Unfortunately we did not have a sufficient amount of sample of high purity to repeat Bridgman's volumetric work.

Phase relations in the system silver–sulfur and the transitions in silver sulfide were investigated by Kracek[6] and reviewed by Frueh[21]. The temperature–composition phase diagram reveals that the III/II transi-

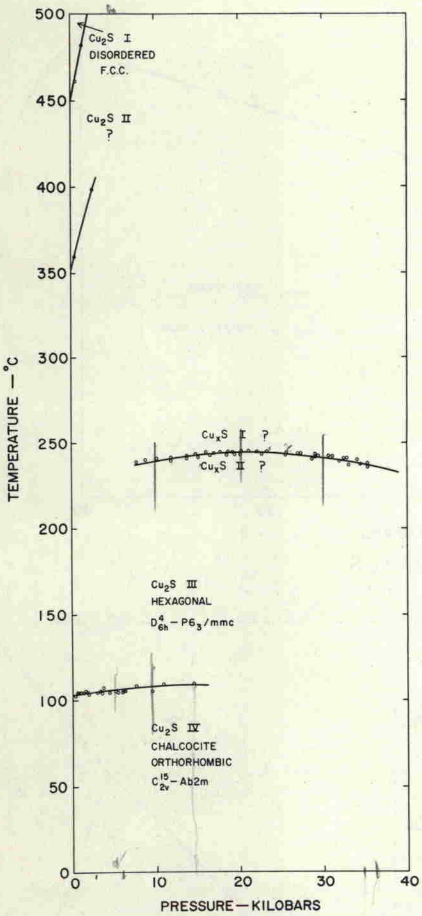

Fig. 5. Phase diagram of Cu_2S with the phase boundary Cu_xS included.

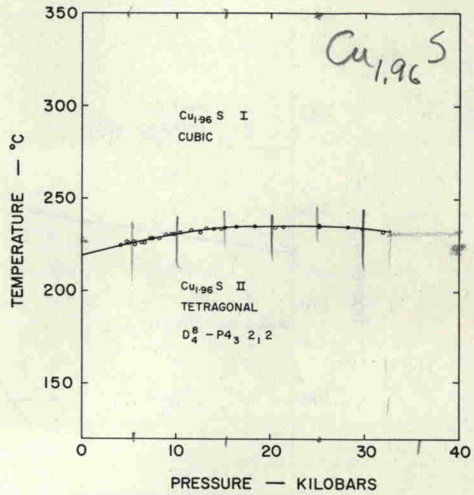

Fig. 6. The I/II phase boundary in $Cu_{1.96}S$.

tion temperature on the silver-rich side is slightly lower than that on the sulfur-rich side (176·3° ± 0·5°C as compared with 177·8° ± 0·7°C). Wagner[22], from EMF measurements on galvanic cells containing solid Ag_2S, concluded that Ag_2S in equilibrium with metallic silver at 200°C contains 2×10^{-3} g atom Ag/mole Ag_2S excess silver whereas Ag_2S in equilibrium with sulfur has nearly the ideal stoichiometric composition. At 160°C the variability in stoichiometry if 3×10^{-5} g atom Ag/mole Ag_2S. He made a thermodynamic calculation to account for the 1·7°C difference between transition temperatures on the Ag-rich and S-rich side. Aside from this small difference the transition temperature does not vary further with excess silver or sulfur, and we consider it safe to have carried out the present experiments on Ag_2S enclosed in silver capsules. The II/I transition is much more sensitive to excess sulfur or silver[6]. We made several attempts to investigate the course of the II/I transition with pressure but encountered a vigorous endothermic sample-capsule reaction above 500°C. This was the only case that such a reaction was encountered, possibly a dissolution of silver in the Ag_2S sample. No such reactions were encountered in the other silver and cuprous chalcogenides at lower temperatures.

Silver selenide

The α/β transformation[8] in Ag_2Se had been studied previously by Roy *et al.*[7] and by Banus[9]. In our experiments we first searched for DTA signals around 130°C, corresponding to the α/β transition. At first no such signals could be obtained, but we found that if the sample was heated in situ to ~ 350°C for a period of several minutes, sharp DTA signals were obtained after the sample had been cooled and another search was made around 130°C. Such signals were then obtained repeatedly four to five times,