

reported to exist at room pressure by Serebrianaia[31] and Jensen[35]. The high pressure points shown were not reproducible and were the only points ever obtained in this region.

Cuprous selenide

The transition in Cu_2Se was reported[32, 33] at 110°C . In our experiments it occurred at 135°C at 1 bar. This is probably due to the high purity of the sample. Preheating in our experiments as required only once for a given sample. Sharp and strong DTA signals were consistently and repeatedly obtained until a pressure of 30 kbars was reached, where the signal disappeared completely. This behavior was reproducible from run to run and was reversible, as the DTA signals were regained upon decompression. We made a thorough search at higher pressure to 41 kbars and found no indication of any further transitions. We postulate that at ~ 30 kbars the transition line intersects a sluggish high pressure phase transition. Unfortunately the lack of a sufficient amount of sample of high purity prevented us from searching for this transition by the piston-displacement method. The course of the phase transition in Cu_2Se with pressure is shown in Fig. 7. Unlike the other

chalcogenides reported here the transition temperature falls with pressure with an initial slope, dT/dp , of $-0.6^\circ\text{C}/\text{kbar}$, and thus implies a negative volume change on passing from the low-temperature tetragonal phase to the high-temperature f.c.c. phase. Crystallographic data[2], on the contrary, yield a positive value for the volume change for Cu_2Se of exact stoichiometry. However, it is impossible to prepare Cu_2Se of stoichiometric composition even by using refined methods[2]. The cell constant of the cubic phase shrinks considerably with copper deficiency[2], and in addition there is some disagreement in the literature as to the exact values of the cell constants of the tetragonal phase[2]. An analogous case of Cu_2S which transforms at 10 kbars by a disproportionation reaction into a copper-deficient phase $\text{Cu}_{1.96}\text{S}$ has been suggested before. Again, at pressures above 24 kbars the transition line in $\text{Cu}_{1.8}\text{S}$ has a negative slope (see Fig. 5 and Fig. 6). An analogous maximum in a solid-solid transition involving a defect structure high temperature b.c.c. phase has been found before in CuCl [34].

The experimentally determined transition points were fitted to cubic equations for interpolation purposes by means of the least mean square method. The results are presented in Table 1.

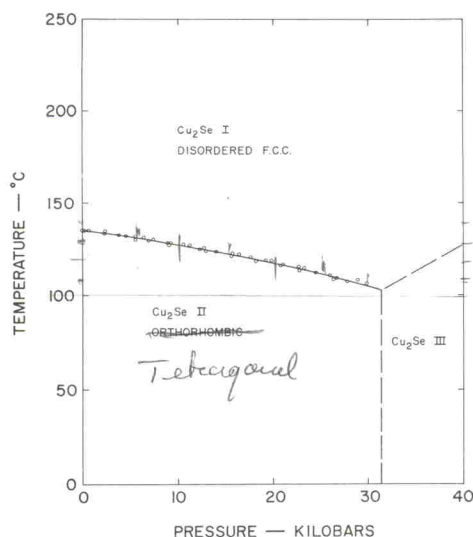


Fig. 7. The phase diagram of Cu_2Se .

Table 1. Phase behavior of Ag_2S , Ag_2Se , Ag_2Te , Cu_2Se and Cu_2S

Transition line	Fit ($^\circ\text{C}$)	Standard deviation ($^\circ\text{C}$)
$\text{Ag}_2\text{Te II/III}$	$t = 143.7 + 11.48P - 0.389P^2$	2.1
$\text{Ag}_2\text{Te II/V}$	$t = 204 + 7.35P - 0.069P^2$	0.8
$\text{Ag}_2\text{Te II/VI}$	$t = 326.6 + 6.51P - 0.053P^2$	0.8
$\text{Ag}_2\text{Se I/II}$	$t = 127 + 6.02P - 0.038P^2$	1.1
$\text{Cu}_2\text{Se I/II}$	$t = 135 - 0.624P - 0.012P^2$	0.8
$\text{Cu}_2\text{S II/III}$	$t = 103.5 + 0.504P - 0.005P^2$	1.2
$\text{Cu}_2\text{S I/II}$	$t = 238.8 + 0.834P - 0.031P^2$	1.2
$\text{Cu}_{1.96}\text{S I/II}$	$t = 219 + 1.56P - 0.036P^2$	0.6
$\text{Ag}_2\text{S II/III}$	$t = 176.7 + 1.57P$	0.8
$\text{Ag}_2\text{S II/IV}$	$t = 195 + 3.13P$	0.7

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Acknowledgements—The authors would like to thank Mrs. Martha C. Pistorius for writing the computer programs used in fitting the data, and Drs. C. W. F. T. Pistorius and R. J. Murphy for valuable discussions. Mr. J. Erasmus and his staff and Mr. G. O'Grady and his staff kept the equipment in good repair, and were responsible for the manufacture of the furnace parts. Calculations were carried out on the IBM System 360/65H of the National Research Institute for Mathematical Sciences.

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