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EFFECT OF PRESSURE ON SOLID-SOLID TRANSITIONS IN SOME SILVER AND CUPROUS CHALCOGENIDES

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Abstract – Phase transitions in Ag₂S, Ag₂Se, Ag₂Te, Cu₂S and Cu₂Se were studied by differential thermal analysis (DTA) to 40 kbar. The transition temperature lines increase with pressure with initial slopes of 1.57, 6, 11.48, and 0.5° C/kbar, respectively, for the first four and -0.6° C/kbar for (probably copper-deficient) Cu₂Se.

INTRODUCTION

THE SILVER and cuprous chalcogenides belong to a class of non-stoichiometric compounds and have interesting electrical properties. Ag₂S, for example, is a semiconductor in its monoclinic room-temperature form and transforms at 177°C into a disordered b.c.c. phase which is a metallic (though poor) conductor[1-3]. The other chalcogenides in this group behave in a similar manner and are also known to undergo phase transformations in the temperature range 100°-200°C [4-5]. The silver and copper chalcogenides are naturally-occurring minerals of some geological interest. Ag₂S in its two modifications (and also Ag₂Se) was suggested to be useful for geologic thermometry [6, 7].

The present work is concerned with phase transformations in these compounds and the dependence of the transition temperatures on pressure. Previously, Roy *et al.*[7] followed the α/β transformations [8] in Ag₂S and Ag₂Se to slightly beyond 1 kbar. More recently, the α/β transformation in Ag₂Se was determined by Banus [9] to 47 kbar in a tetrahedral anvil press and, very recently, Banus and Finn [10] determined the phase diagram of Ag₂Te to 25 kbar and 250°C in a hydrostatic apparatus.

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EXPERIMENTAL

Ag₂S of stated purity of 99·99%, and Ag₂Se and Ag₂Te both of stated purity of 99·999% were obtained from Koch-Light Laboratories. Cu₂S and Cu₂Se were obtained from Rocky Mountain Chemicals and were of stated purity of 99% and 99·99%, respectively. The quantities of these substances that were available were sufficient for several differential thermal analysis (DTA) experiments on each substance but not for volumetric (*P-V-T*) work.

Quasihydrostatic pressures to 40 kbar were generated in a piston-cylinder device previously described [11, 12]. The furnace assembly was similar to that described by Cohen et al.[13]. Phase transitions were detected by means of differential thermal analysis (DTA)[11, 14] with Chromel-Alumel thermocouples. The heating rate was usually in the range 0.8-2.5°C/sec. Corrections were made for the effect of pressure on the thermocouples[15]. The corrections are, however, quite small in the temperature range of present experiments. The silver compounds were contained in silver capsules and the copper compounds in copper capsules. The capsule design, incorporating a thermocouple well, had been previously described [16]. The longitudinal temperature gradient along the sample capsule was reduced by sandwiching the capsule

between two insulated copper plugs [17]. Sliding friction was determined and corrected for by comparing results obtained on increasing and decreasing pressure [14]. The pressures obtained in this way were further corrected for the effect of nonsymmetrical pressure loss [18]. The corrected pressures are believed accurate to ± 0.5 kbar. Temperatures could be determined to $\pm 1^{\circ}-2^{\circ}C$. Each phase boundary (in a pressure temperature diagram, as the results are presented here) is based on at least four repeated determinations on different samples with consistency of 1°-2°C. The procedure for following phase transitions (and correcting for friction) below ~ 4 kbar has been described elsewhere [19].

RESULTS AND DISCUSSION

Typical DTA signals obtained for some of the transitions studied here are presented in Fig. 1. Experimental results are presented in Figs. 2-6 in the form of temperature-pressure (phase) diagrams. A line in such a p-T diagram, drawn through the experimentally determined transition points, divides the p-T plane into the regions of stability of the two phases and is referred to in the following discussion as a phase boundary or transition line. The points plotted in the p-T diagrams are the averages between transition temperatures on heating and on cooling.

Silver sulphide

The phase diagram of Ag₂S to 40 kbar and 300°C is shown in Fig. 2. The III/II (Kracek's notation[6]) transition temperature increases linearly with pressure with a slope of 1.5 $\pm 0.2°C$ /kbar. The initial slope estimated previously by Roy *et al.*[7] as ~4°C/kbar seems somewhat too high and might be open to question due to the very limited pressure range, viz. ~ 1.2 kbar, and the large hysteresis interval in their experiments. The hysteresis interval in our experiments was slight, ~ 1°C, up to the highest pressure attained. Above 12.3 kbars, 195°C the transition line lies on another straight line section



Fig. 1. Typical DTA signals. (i) Signal at $6\cdot 3$ kbars, $226\cdot 5^{\circ}C$ on the Cu_{1.96}S I/II boundary. (ii) Signal at $32\cdot 9$ kbars, 283·5°C on the Ag₂Se I/II boundary. (iii) Signal at $6\cdot 4$ kbars, 131°C on the I/II boundary in Cu₂Se. (iv) (a) Signal at $6\cdot 1$ kbars, $105\cdot 5^{\circ}C$ on the I/III boundary in Cu₂Se. (b) Signal at $13\cdot 9$ kbars, $242\cdot 5^{\circ}C$ on the Cu_xS I/II boundary. (v) (a) Ag₂Te on the V/II boundary at $25\cdot 7$ kbars and $316\cdot 2^{\circ}C$. (b) Ag₂Te on the V/II boundary at $28\cdot 8$ kbars and $332\cdot 5^{\circ}C$.

with a different slope, viz. $3 \cdot 1 \pm 0 \cdot 2^{\circ}$ C/kbar. The III/IV transition line determined by Bridgman[20] from 100° to 200°C is also shown in Fig. 2. The only break in the III/II trajectory that might indicate the occurrence

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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

Fig. 4. Phase diagram to 400°C and 40 kbars of Ag₂Te (including the work by Banus and Finn).

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-

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

tion temperature on the silver-rich side is slightly lower than that on the sulfur-rich side ($176 \cdot 3^{\circ} \pm 0 \cdot 5^{\circ}$ C as compared with $177 \cdot 8^{\circ} \pm$ $0 \cdot 7^{\circ}$ C). Wagner [22], from EMF measurements on galvanic cells containing solid Ag₂S, concluded that Ag₂S in equilibrium with metallic silver at 200°C contains 2×10^{-3} g atom Ag/ mole Ag₂S excess silver whereas Ag₂S 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 Ag₂S. He made a thermodynamic calculation to account for the $1 \cdot 7^{\circ}$ C difference between transition temperatures on the Agrich and S-rich side. Aside from this small



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

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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 Ag₂Se 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,

gradually diminishing in size. Repeating such preheating procedure reproduced this behavior. No such preheating was necessary above $\sim 6 \text{ kbar}$ 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 Ag₂S, 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 Ag₂Se is not known.

The phase diagram of Ag₂Se 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 $7 \cdot 2^{\circ}$ C/kbar reported by Roy *et al.* [7] as in the case of Ag₂S. The agreement with Banus's data below 20 kbar shows that our preheating treatment did not change the Ag₂Se 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 Ag₂Se, and, similarly, was unnecessary above ~ 6 kbars. Ag₂Te 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 Ag₂Se, 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 $145^{\circ} \pm 3^{\circ}$ C, whereas on the silver-deficient side complicated behavior due to coexistence of $Ag_{5-x}Te_3$, Ag_2Te and $a\gamma$ -phase was reported by Kracek and Ksanda[25]. The prehating treatment that we used thus ensured equilibrium of Ag₂Te with excess Ag, as is also apparent from our 1 bar value of $147^{\circ} \pm 1^{\circ}$ C. The latter value compares favorably with that of Kracek et al. [23] and also with the recent value of $148^{\circ} \pm 1^{\circ}$ 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 cooling (II/III) took place some 20°C lower than on heating (III/II), vielding 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, Ag₂TeVI. 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 Ag₂Te 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 coppersulfur 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 Cu₂S, 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 Cu₂S and free

copper. Our samples, enclosed in copper capsules and given a preheating treatment at 380°C were, therefore, in the Cu₂S 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 Cu₂S to 900°C. We therefore heated Cu₂S 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 $\sim 10^{\circ}$ 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 Cu₂S. Both Cu₉S₅ samples formed in situ in the presence of Cu and Cu₂S are probably not very pure, and hence the 10°C difference in transition temperatures.

The temperature-hysteresis interval in the case of Cu₂S 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 Cu₂S III/II and II/I transitions were

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 Cu₂Se 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 Cu₂Se with pressure is shown in Fig. 7. Unlike the other



Fig. 7. The phase diagram of Cu₂Se.

chalcogenides reported here the transition temperature falls with pressure with an initial slope, dT/dp, of $-0.6^{\circ}C/kbar$, 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 Cu₂Se of exact stoichiometry. However, it is impossible to prepare Cu₂Se of stoichiometric composition even by using refined methods [2]. The cell constant of the cubic phase shrinks considerably with copper deficency [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 Cu₂S which transforms at 10 kbars by a disproportionation reaction into a copper-deficient phase Cu_{1.96}S has been suggested before. Again, at pressures above 24 kbars the transition line in Cu_{1.8}S has a negative slope (see Fig. 5 and Fig. 6). An analogous maximum in a solidsolid 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.

Table 1. *Phase behavior of* Ag₂S, Ag₂Se, Ag₂Te, Cu₂Se *and* Cu₂S

Transition line	Fit (°C)	Standard deviation (°C)
Ag ₂ Te II/III	$t = 143.7 + 11.48P - 0.389P^2$	2.1
Ag ₂ Te II/V	$t = 204 + 7 \cdot 35P - 0 \cdot 069P^2$	0.8
Ag ₂ Te II/VI	$t = 326 \cdot 6 + 6 \cdot 51P - 0 \cdot 053P^2$	0.8
Ag ₂ Se I/II	$t = 127 + 6 \cdot 02P - 0 \cdot 038P^2$	1.1
Cu ₂ Se I/II	$t = 135 - 0.624P - 0.012P^2$	0.8
Cu ₂ S II/III	$t = 103 \cdot 5 + 0 \cdot 504P - 0 \cdot 005P^2$	1.2
Cu _x S I/II	$t = 238 \cdot 8 + 0 \cdot 834P - 0 \cdot 031P^2$	1.2
Cu1.96S I/II	$t = 219 + 1.56P - 0.036P^2$	0.6
Ag ₂ S II/III	$t = 176 \cdot 7 + 1 \cdot 57P$	0.8
Ag ₂ S II/IV	t = 195 + 3.13P	0.7

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