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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 Ag_2S, Ag_2Se, Ag_2Te, Cu_2S and Cu_2Se 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) Cu_2Se.

INTRODUCTION

THE SILVER and cuprous chalcogenides belong to a class of non-stoichiometric compounds and have interesting electrical properties. Ag_2S, 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. Ag_2S in its two modifications (and also Ag_2Se) 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 Ag_2S and Ag_2Se to slightly beyond 1 kbar. More recently, the α/β transformation in Ag_2Se 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 Ag_2Te to 25 kbar and 250°C in a hydrostatic apparatus.

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EXPERIMENTAL

Ag_2S of stated purity of 99·99%, and Ag_2Se and Ag_2Te both of stated purity of 99·999% were obtained from Koch-Light Laboratories. Cu_2S and Cu_2Se 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 $\pm 0{\cdot}5$ kbar. Temperatures could be determined to $\pm 1°$–$2°$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 Ag_2S 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 $1{\cdot}5 \pm 0{\cdot}2$°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. $\sim 1{\cdot}2$ 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

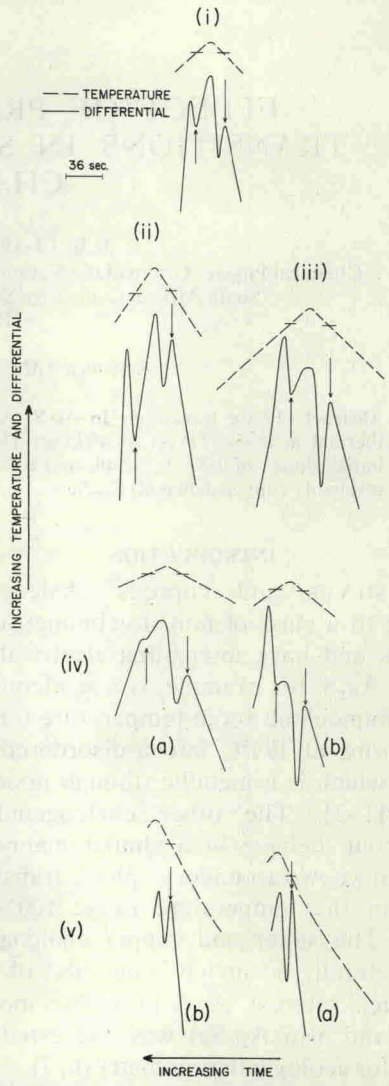

Fig. 1. Typical DTA signals. (i) Signal at 6·3 kbars, 226·5°C on the $Cu_{1{\cdot}96}S$ I/II boundary. (ii) Signal at 32·9 kbars, 283·5°C on the Ag_2Se I/II boundary. (iii) Signal at 6·4 kbars, 131°C on the I/II boundary in Cu_2Se. (iv) (a) Signal at 6·1 kbars, 105·5°C on the I/III boundary in Cu_2S. (b) Signal at 13·9 kbars, 242·5°C on the Cu_xS I/II boundary. (v) (a) Ag_2Te on the V/II boundary at 25·7 kbars and 316·2°C. (b) Ag_2Te on the VI/II boundary at 28·8 kbars and 332·5°C.

with a different slope, viz. $3{\cdot}1 \pm 0{\cdot}2$°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