

and to Dr. H. W. Radmacher in whose laboratory the spectrochemical determinations were carried out.

## REFERENCES

- GAUDEFRY, C., C. JOURAVSKY AND F. PERMINGEAT (1963) La marokite,  $\text{CaMn}_2\text{O}_4$ , une nouvelle espèce minérale. *Bull. Soc. Franç. Mineral. Cristallogr.* **86**, 359-367.
- LEPICARD, G., AND J. PROTAS (1966) Étude structurale de l'oxyde double de manganèse et de calcium orthorhombique  $\text{CaMn}_2\text{O}_4$ . *Bull. Soc. Franç. Mineral. Cristallogr.* **89**, 318-324.
- RIBOUD, P. V. AND A. MUAN (1963) Melting relations of CaO-manganese oxide and MgO—manganese oxide mixtures in air. *J. Amer. Ceram. Soc.* **46**, 33-36.
- VILLIERS, P. R. DE AND F. H. HERBSTEIN (1967) Distinction between two members of the braunite group. *Amer. Mineral.* **52**, 20-30.

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THE SYSTEM  $\text{Ag}_3\text{AuS}_2\text{-Ag}_2\text{S}$ 

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## INTRODUCTION

A considerable number of investigations have been conducted on the silver chalcogenides due to interest in their electrical properties. The system  $\text{Cu}_2\text{S-Ag}_2\text{S}$  has been examined in detail (Skinner, 1966) because several compounds in this system occur as ore minerals, and also because a portion of the system contains compounds which have interesting electrical properties (Graf, 1967). In contrast, very little information is available concerning the system Ag-Au-S. As a consequence, after completing an investigation of the electrical properties of a portion of the system  $\text{Cu}_2\text{S-Ag}_2\text{S}$ , a brief investigation was conducted on the system  $\text{Ag}_3\text{AuS}_2\text{-Ag}_2\text{S}$ , resulting in the determination of the eutectoid phase diagram from room temperature up to 200°C.

## EXPERIMENTAL PROCEDURE

The various compounds were formed by sintering the elements (99.999% purity) in evacuated and sealed glass tubes until none of the free elements remained. The preparation of the desired compounds was then verified by powder X-ray diffraction. The samples for measurements were obtained by filing powders from the sintered ingots. The measurements were made by D. T. A. and by electrical resistivity methods. The D.T.A. apparatus consisted of a Kanthal-wound furnace heated by a motor-driven variac, a Hewlett-Packard model 425A microvolt-ammeter for amplifying the signal from the differential thermocouple, and a Moseley x-y recorder for recording the signals. The sample holder was made of pyrophyllite which is easily machined and is suitable for low temperature use. A heating rate of 10°/min was employed for the D.T.A. The electrical resistivity measurements were made on samples which were fabricated by pressing the powders into pellets. These

powder compacts, 0.250 inch in diameter, and 0.125 inch long, were pressed in a split die constructed in a manner which made it possible to press a chromel-alumel thermocouple into the center of the pellet. Aquadag electrodes were then applied to the samples. Because of the ionic conductivity in silver sulfide, the resistivity measurements were made with alternating current. A constant, 60 cycle current of 100 milliamperes was passed through the samples and the voltage change was measured as a function of temperature. The voltage was measured with a Moseley log converter and the output of the log converter was plotted against the thermocouple voltage on the x-y recorder. The proper calibration then gave a plot of the log of the sample resistance versus temperature. The compositions which were made up corresponded to 8, 20, 32, 44, 52, 60, 80, 92 and 100 mole %  $\text{Ag}_3\text{AuS}_2$  and sufficient  $\text{Ag}_2\text{S}$  to make 100 mole %.

### EXPERIMENTAL RESULTS

The nature of the data obtained from these samples is such that at an invariant point, for example at a eutectoid point or a phase transformation in a compound, only one reaction will be detected, while at all other compositions the data will resemble that shown in Figure 1. The upper curve in Figure 1 is a plot of the log of the resistance versus temperature of a sample as it was heated at a rate of  $4^\circ/\text{min}$ . This curve first shows the

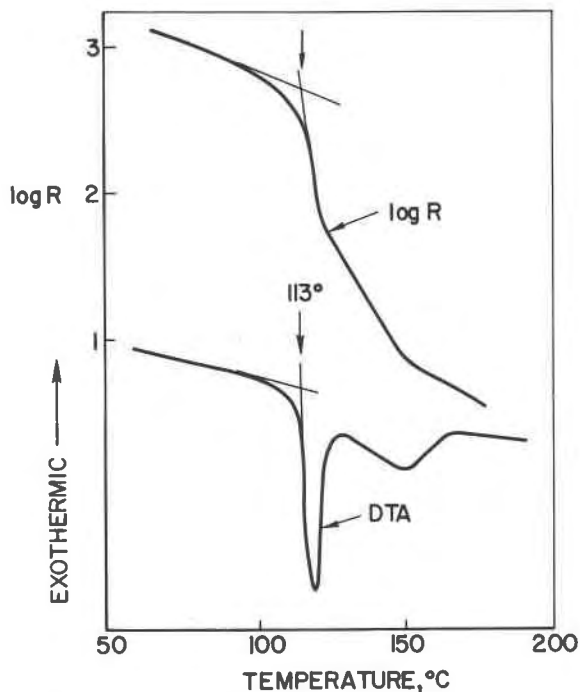


FIG. 1. Electrical resistance and D. T. A. curves for the composition 20%  $\text{Ag}_3\text{AuS}_2$ -80%  $\text{Ag}_2\text{S}$ .

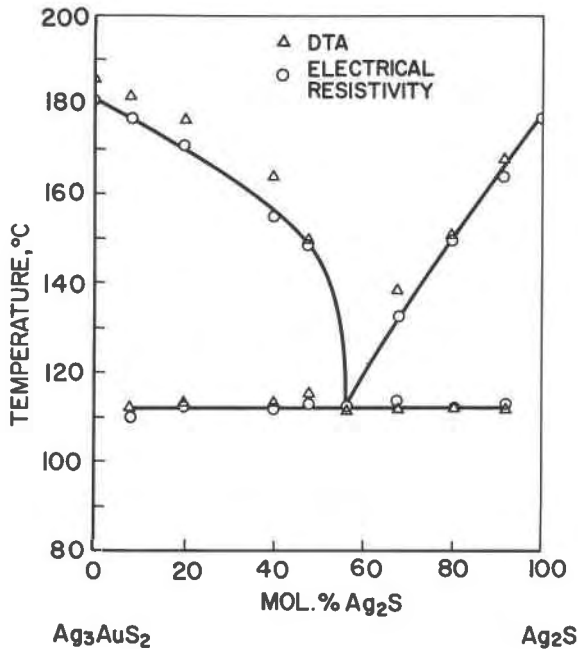


FIG. 2. The system  $\text{Ag}_3\text{AuS}_2\text{-Ag}_2\text{S}$ .

decreasing resistance of a mixture of  $\text{Ag}_3\text{AuS}_2$  and acanthite ( $\text{Ag}_2\text{S}$ ) as the temperature was raised, next the sharp drop in resistance at the eutectoid temperature ( $113^\circ \pm 1^\circ$ ), then the decreasing resistance as  $\text{Ag}_2\text{S}$  and the argentite solid solution react, and finally the decreasing resistance of the high temperature solid solution with increasing temperature. The diagram in Figure 2 was constructed from the points at which the first and third changes in slope occurred. These points correspond to the beginning of the eutectoid reaction and the end of the reaction between the high temperature solid solution and acanthite ( $\text{Ag}_2\text{S}$ ) or  $\text{Ag}_3\text{AuS}_2$ . The precise temperatures for these changes in slope were obtained by extrapolating the straight line portions of the curve on either side of the transformation temperature, as shown in Figure 1. The D.T.A. curve (Fig. 1) shows the same reaction sequence. There is a well defined endothermic peak which begins at  $113^\circ \pm 1^\circ$ , and next a continuing endothermic reaction as  $\text{Ag}_2\text{S}$  and the high temperature solid solution react and then a return to the baseline when this reaction is completed. The baseline is not parallel to the temperature axis, but the reactions are clearly indicated. At the transformation temperatures of  $\text{Ag}_2\text{S}$  and  $\text{Ag}_3\text{AuS}_2$ , and at the eutectoid point, there is only one peak, just as the resistance curve shows only one

reaction at these points. The D.T.A. data points on the left side of figure 2 occur at a few degrees higher temperature than do the points obtained by resistivity methods. This discrepancy is caused by taking these data points from the D.T.A. curves at the temperature at which the curve begins to return to the baseline. This procedure was followed because for some compositions only the first peak, at the eutectoid temperature, was well defined. For the composition 92%  $\text{Ag}_3\text{AuS}_2$ -8%  $\text{Ag}_2\text{S}$  and the compound  $\text{Ag}_3\text{AuS}_2$  a well-defined peak existed near the high temperature end of the curve, and by taking the beginning of these peaks, as was done for the eutectoid temperatures (Fig. 1), the data fell on the same curve as that from the resistance measurements. For this reason the phase boundaries in Figure 2 are drawn through the data points obtained from the resistance data. All of the data were taken with increasing temperature,

TABLE 1. X-RAY DIFFRACTION DATA FOR  $\text{Ag}_3\text{AuS}_2$ 

<i>hkl</i>	Estimated Intensity	Observed <i>d</i> , Å	Calculated <i>d</i> , Å
110	80	6.98	6.90
210	60	4.38	4.36
211	10	3.99	3.99
220	20	3.46	3.45
300	30	3.25	3.25
310	60	3.09	3.08
311	30	2.943	2.943
222	60	2.809	2.825
203	100	2.731	2.724
321	90	2.609	2.609
322	30	2.371	2.371
410			2.365
114	20	2.319	2.320
411	10	2.297	2.300
330			2.298
331	30	2.236	2.238
214	50	2.147	2.146
421	80	2.124	2.129
224	10	2.011	2.004
422	50	1.992	1.994
105	40	1.925	1.932
333	20	1.885	1.883
520	50	1.807	1.811
521	40	1.780	1.781
404	10	1.735	1.733
530	10	1.669	1.672
216	20	1.536	1.537
622	30	1.470	1.472
326	30	1.406	1.404

because the high temperature compounds tended to supercool several degrees.

Although the exact composition of  $\text{Ag}_3\text{AuS}_2$  was not determined, the measurements on the compound formed from appropriate amounts of reactants required to produce this composition revealed only a single reaction, and powder X-ray diffraction photographs of the compound resulted in a pattern all the lines of which could be indexed on a tetragonal unit cell, with  $a=9.75 \text{ \AA}$  and  $c=9.85 \text{ \AA}$ . The X-ray data are presented in Table 1.

#### SUMMARY

The portion of the Ag-Au-S phase diagram between  $\text{Ag}_3\text{AuS}_2$  and acanthite ( $\text{Ag}_2\text{S}$ ) from room temperature up to  $200^\circ\text{C}$  has been determined by using D.T.A. and electrical resistivity methods. The experimental results suggest that electrical resistivity methods may be applicable in some instances for the study of solid-solid phase boundaries, particularly those in which the high-temperature phase cannot be quenched. The results obtained by D.T.A. are less exact, but are adequate and the method may be applicable to a greater variety of materials. The data indicate the existence of  $\text{Ag}_3\text{AuS}_2$ , a phase transformation in  $\text{Ag}_3\text{AuS}_2$  at  $181^\circ$ , and a eutectoid reaction between  $\text{Ag}_3\text{AuS}_2$  and  $\text{Ag}_2\text{S}$  at approximately 56%  $\text{Ag}_2\text{S}$ -44%  $\text{Ag}_3\text{AuS}_2$  which occurs at  $113^\circ$ . The compound  $\text{Ag}_3\text{AuS}_2$  has not been reported as a mineral and is not isostructural with the minerals petzite ( $\text{Ag}_3\text{AuTe}_2$ ) or jalpaite ( $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ ). The powder X-ray data for  $\text{Ag}_3\text{AuS}_2$  are presented.

#### ACKNOWLEDGEMENT

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#### REFERENCES

- GRAF, R. B. (1967) Phase transformations in the system  $\text{Cu}_2\text{S}$ - $\text{Ag}_2\text{S}$ . *J. Electrochem. Soc.* (in press).  
SKINNER, B. J. (1966) The system Cu-Ag-S. *Econ. Geol.*, **61**, 1-26.