

## Silver(I) sulfide: Ag<sub>2</sub>S

### Heat capacity from 5 to 1000 K, thermodynamic properties, and transitions<sup>a</sup>

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The heat capacity of Ag<sub>2</sub>S has been measured by adiabatic-shield calorimetry from 5 to 1000 K. The heat capacity increases regularly up to about 445 K where the pre-transitional contribution causes rapidly rising values. The  $\alpha$ -to- $\beta$  transition of Ag<sub>2</sub>S occurs in the range 449.3 to 451.3 K, depending upon previous history of the sample. The enthalpy of transition  $\Delta_{\text{trs}}H_m = (4058 \pm 26) \text{ J} \cdot \text{mol}^{-1}$ . A slightly decreasing heat capacity is observed for  $\beta$ -Ag<sub>2</sub>S from 88.1 J·K<sup>-1</sup>·mol<sup>-1</sup> at 460 K to 85.0 J·K<sup>-1</sup>·mol<sup>-1</sup> at 850 K with a minimum of 84.6 J·K<sup>-1</sup>·mol<sup>-1</sup> at 750 K. The transition of  $\beta$ -Ag<sub>2</sub>S to  $\gamma$ -Ag<sub>2</sub>S occurs at about 865 K with  $\Delta_{\text{trs}}H_m = (784 \pm 5) \text{ J} \cdot \text{mol}^{-1}$ . Thermodynamic functions have been evaluated and the values of  $C_{p,m}$ ,  $\{S_m^\circ(T) - S_m^\circ(0)\}$ , and  $-\{G_m^\circ(T) - H_m^\circ(0)\}/T$  at 298.15 K are 75.31, 142.89, 85.43, and at 1000 K are 80.57, 253.28, 172.77 J·K<sup>-1</sup>·mol<sup>-1</sup>, respectively. No signs of further transitions were found, either in the stoichiometric compound, or in a sample with overall composition Ag<sub>2</sub>S<sub>1.0526</sub>. Thus, the present work does not support the hypothesis of Perrott and Fletcher concerning partial disordering of stoichiometric Ag<sub>2</sub>S around 600 K as opposed to complete disordering around 450 K in the presence of excess silver or sulfur. Subtraction of the estimated lattice heat capacity at constant pressure leaves a large transitional heat capacity for  $\beta$ -Ag<sub>2</sub>S above 450 K. It is about 11 J·K<sup>-1</sup>·mol<sup>-1</sup> at 500 K and decreases gradually to about 6 J·K<sup>-1</sup>·mol<sup>-1</sup> at 850 K. Its origin is discussed.

## 1. Introduction

The only well characterized solid compound of silver and sulfur is silver(I) sulfide: Ag<sub>2</sub>S. It exists under ordinary pressure in three well-defined crystalline modifications, usually designated  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Ag<sub>2</sub>S, with  $\alpha$ -Ag<sub>2</sub>S as the low-temperature phase. The heat capacity of these silver(I) sulfide phases has been

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studied repeatedly in recent years, partly with surprising outcome. The results for  $\alpha$ -Ag<sub>2</sub>S by Gulyaev and Petrov<sup>(1)</sup> in the region 80 to 300 K were superseded by those of higher accuracy from Walsh *et al.*<sup>(2)</sup> over the region 10 to 300 K. Overlapping results were obtained by Jost and Kubaschewski<sup>(3)</sup> in the range 200 to 300 K, and the regularly rising trend continued up to 370 K. With further rise in temperature, an increasing defect-formation contribution to the heat capacity of  $\alpha$ -Ag<sub>2</sub>S was observed. The actual  $\alpha$ -to- $\beta$  transition occurs at about 450 K and the heat capacity of  $\beta$ -Ag<sub>2</sub>S was found to decrease from 90 to 88 J·K<sup>-1</sup>·mol<sup>-1</sup> over the range 460 to 620 K.

In contrast to the latter result, Perrott and Fletcher<sup>(4)</sup> observed a rising heat capacity for stoichiometric  $\beta$ -Ag<sub>2</sub>S in the same temperature range and a rapid fall to a constant value of about 92 J·K<sup>-1</sup>·mol<sup>-1</sup> above 620 K. This was interpreted in terms of structural lattice disordering of the silver atoms. Strangely enough, the effect occurred only for a stoichiometric sample, while two other samples with an excess of 0.01 in the mole fraction of either Ag or S failed to show the  $\lambda$ -type transition in the 600 K region. The enthalpy increment of the  $\alpha$ -to- $\beta$  transition was, however, found to be correspondingly larger in the non-stoichiometric samples:  $\Delta_{\text{trs}}H_m = (6.5 \pm 0.4)$  kJ·mol<sup>-1</sup>, than in the stoichiometric one:  $\Delta_{\text{trs}}H_m = (4.0 \pm 0.4)$  kJ·mol<sup>-1</sup>.

Perrott and Fletcher's<sup>(4)</sup> claim that their results were consistent with partial disordering of stoichiometric Ag<sub>2</sub>S above the  $\alpha$ -to- $\beta$  transition temperature was a consequence of their observation of a monotonically increasing—and rather irreproducible—heat capacity, culminating in an additional transition at 620 K, in contrast to the low and essentially constant heat capacities above 450 K for samples annealed in the presence of excess silver or sulfur.

The authors have repeated and extended the heat-capacity measurements on a well-characterized silver(I) sulfide sample in order to ascertain whether the peculiar behavior reported by Perrott and Fletcher<sup>(4)</sup> for stoichiometric Ag<sub>2</sub>S could be confirmed. A sample with some excess of sulfur was also prepared and measured for comparison.

Information about compositional differences and extension of the homogeneity ranges of the three silver(I) sulfide phases is plentiful. Thus, Kracek<sup>(5)</sup> observed a 1.5 K shift in the  $\alpha$ -to- $\beta$  transition temperature from the silver-rich to the sulfur-rich side. Later studies by Schmalzried and Reye<sup>(6-8)</sup> have shown that for  $\alpha$ -Ag<sub>2+ $\delta$</sub> S the value of  $\delta$  is in the range  $\pm 6 \times 10^{-6}$  just below the transition temperature (450 K). For  $\beta$ -Ag<sub>2+ $\delta$</sub> S the variability is much larger, and is already in the range  $0.0001 < \delta < 0.002$  close to the same temperature. The 40 K shift for the  $\beta$ -to- $\gamma$  transition of Ag<sub>2+ $\delta$</sub> S around 870 K with the sulfur content, reported by Kracek,<sup>(5)</sup> was related by Rau<sup>(9)</sup> to a compositional variation of  $\beta$ -Ag<sub>2+ $\delta$</sub> S from  $\delta = +0.005$  to  $-0.015$  in this temperature range. An even larger composition range was derived for  $\gamma$ -Ag<sub>2+ $\delta$</sub> S by Rau<sup>(9)</sup> ( $\delta_{\text{min}} = -0.020$  at 1017 K,  $\delta_{\text{max}} = 0.015$  at 1081 K).

Furthermore, the energetics of the transitions need to be related to the structural changes in the silver(I) sulfides. According to Frueh<sup>(10)</sup> and Sadanaga and Sueno<sup>(11)</sup> the monoclinic structure of  $\alpha$ -Ag<sub>2</sub>S, achantite, can be described as a slightly distorted body-centered cubic structure with two types of silver atoms in equal

amounts, occupying octahedral and tetrahedral interstices between the sulfur atoms. The coordination polyhedra are considerably distorted.

The sulfur-atom arrangement is practically unchanged in the transition to body-centered cubic  $\beta\text{-Ag}_2\text{S}$ . In the early structural study by Rahlfs<sup>(12)</sup> the silver ions were assumed to be randomly distributed over 6 octahedral, 12 tetrahedral, and 24 triangular interstices. According to the single-crystal neutron-diffraction study by Cava *et al.*<sup>(13)</sup> in the range 460 to 600 K, the silver ions are confined to the tetrahedral interstices at 530 K and above, while at temperatures approaching the lower limit for  $\beta\text{-Ag}_2\text{S}$ , about 1/5 of the silver atoms are located in the octahedral interstices. In the transition of  $\beta\text{-Ag}_2\text{S}$  to  $\gamma\text{-Ag}_2\text{S}$  the structure changes from body-centered to face-centered cubic according to Djurle<sup>(14)</sup> and Frueh,<sup>(15)</sup> and likewise according to Skinner,<sup>(16)</sup> who inferred that the structure was identical to the f.c.c. form of  $\text{Cu}_2\text{S}$ .

Phenomenological theories applicable to the transition of  $\alpha\text{-Ag}_2\text{S}$  to the fast-ion conductor  $\beta\text{-Ag}_2\text{S}$  have been developed in terms of the mean-field approximation by Gurevich and Kharkats,<sup>(17)</sup> and of the single-valued dependence of defect formation energy and entropy on the crystal volume by Schmalzried.<sup>(18)</sup> The transitional heat capacity of  $\alpha\text{-Ag}_2\text{S}$  and  $\beta\text{-Ag}_2\text{S}$  are re-evaluated and compared with these theories.

## 2. Experimental

### SAMPLE PREPARATION

Silver(I) sulfide was synthesized from high-purity silver and sulfur. The >99.99 mass per cent purity silver shot was from the American Smelting and Refining Company, N.J., U.S.A. It was reported to contain the following impurities (mass fraction  $\times 10^6$ ): Bi, <1; Cu, 8; Fe, 3; Pb, <1. No other elements were detected. The >99.999 mass per cent purity sulfur from the same source was reported to contain mass fractions less than  $1 \times 10^{-6}$  of Cl and Na, while no Ag, Al, Bi, Ca, Cd, Cr, Cu, Fe, In, Mg, Mn, Ni, Pb, Sb, Si, Sn, or Zn were detected by standard spectrographic methods.

The mixture of the elements was heated in an evacuated silica-glass tube from 360 to 480 K over a period of 6 d, and was afterwards kept at 590, 670, and 770 K for 3, 1, and 1 d, respectively. It was then cooled to 300 K in the furnace. Duplicate silver analyses by hydrogen reduction of the shiny black sulfide at 1100 K gave 87.05 and 87.03 mass per cent of Ag (theoretical: 87.06) after a slight adjustment for silver evaporation.

The stoichiometry of the sample was changed after completion of the measurements by adding 1.074 g of sulfur to 157.80 g of stoichiometric  $\text{Ag}_2\text{S}$  in a sample container of fused silica. The sample was heated at 620 K for 24 h in sealed condition and then cooled with the furnace.

X-ray photographs of the  $\text{Ag}_2\text{S}$ -sample were taken in a Guinier-type camera of 80 mm diameter. Cu ( $K\alpha_1$ ) radiation was used with KCl as a calibration substance for which  $a(293 \text{ K}) = 629.19 \text{ pm}$ .<sup>(19)</sup> The structure of  $\alpha\text{-Ag}_2\text{S}$  is monoclinic, and the orientation by Sadanaga and Sueno<sup>(11)</sup> is chosen here as it facilitates comparison with the cubic high-temperature structure. The orientation corresponds to the

standard setting of the space group  $C_{5h}^2$  ( $P2_1/c$ ), while Ramsdell<sup>(20)</sup> chose  $B2_1/c$  and Frueh<sup>(10)</sup> chose  $P2_1/n$ . The derived cell dimensions are (the figures in parentheses indicate one standard deviation in the last digit):  $a = 423.1(1)$ ,  $b = 692.7(1)$ ,  $c = 953.2(2)$  pm,  $\beta = 125.65(1)^\circ$ , in good agreement with earlier findings by Djurle:<sup>(14)</sup>  $a = 422.5$ ,  $b = 692.5$ ,  $c = 953.1$  pm,  $\beta = 125.59^\circ$ , by Frueh:<sup>(10)</sup>  $a = 423$ ,  $b = 691$ ,  $c = 953$  pm,  $\beta = 125.52^\circ$ , by Swanson *et al.*:<sup>(21)</sup>  $a = 422.9$ ,  $b = 693.1$ ,  $c = 952.9$  pm,  $\beta = 125.56^\circ$ , and by Sadanaga and Sueno:<sup>(8)</sup>  $a = 423.1$ ,  $b = 693.0$ ,  $c = 952.6$  pm,  $\beta = 125.48^\circ$ . Only one very weak line at  $\sin^2\theta = 0.10677$  on the X-ray photograph remained unidentified in the range up to  $\sin^2\theta = 0.28$ . The lattice constants of  $Ag_2S_{1.0526}$  were found to be equal to those of  $Ag_2S$  within the limits of error.

### CALORIMETRIC TECHNIQUE

5 to 350 K, *University of Michigan*. Heat-capacity measurements were made in the Mark (II) adiabatic cryostat, which has been described previously.<sup>(22)</sup> The sample was contained in a gold-plated copper calorimeter (laboratory designation W-54) which incorporated a gold-gasketed seal and gold-plated copper vanes to enhance conduction. The calorimeter had a mass of 42 g and an internal volume of 80 cm<sup>3</sup>. To facilitate rapid thermal equilibration, a small amount of helium gas was introduced. The temperature of the calorimeter was measured with a platinum capsule-type 25  $\Omega$  (nominal) resistance thermometer (laboratory designation A-5) inserted into a re-entrant well in the calorimeter.

The sample was loaded into the calorimeter under an atmosphere of nitrogen in a dry-box. The stainless-steel vessel containing the calorimeter was connected to a high-vacuum line and after evacuation a small amount of helium gas was admitted (2.5 kPa at 300 K). The calorimeter was then sealed, placed in the cryostat, and cooled.

300 to 1000 K, *University of Oslo*. The calorimetric apparatus and measuring techniques have been described.<sup>(23)</sup> The calorimeter was intermittently heated and surrounded by electrically heated and electronically controlled adiabatic shields. The substance was enclosed in an evacuated and sealed silica-glass tube of about 50 cm<sup>3</sup> volume, tightly fitted into the silver calorimeter. A central well in the tube served for the heater and platinum resistance thermometer.

*Calibrations.* The platinum-resistance thermometer for the low-temperature calorimeter was calibrated by the U.S. National Bureau of Standards, and that for the high-temperature calorimeter locally, at the ice, steam, tin, zinc, and antimony points. Temperatures are judged to correspond to IPTS-68 within 0.03 K from 5 to 300 K and within 0.05 K between this temperature and 900 K. The uncertainty rises to 0.2 K at 1000 K. Resistance, energy, and mass were measured with reference to instruments calibrated by the U.S. National Bureau of Standards. The heat capacities of the empty calorimeters were determined in separate series of experiments. The heat capacity of the sample was about 98 per cent of the total in

the low-temperature calorimeter at 10 K, 83 per cent at 50 K, and 71 per cent above 100 K, and about 40 per cent in the high-temperature calorimeter.

Small corrections were applied for temperature excursions of the shields from the calorimeter temperature and for "zero drift" of the calorimeter temperature. Further small corrections were applied for differences in amounts of helium gas and Apiezon-T grease for the low-temperature calorimeter and for differences in mass of the silica-glass containers for the high-temperature calorimeter. The mass of Ag<sub>2</sub>S sample used in the calorimeters was about 160 g.

### 3. Results

The experimental heat capacities for the low- and high-temperature ranges are given in table 1 and the transitional enthalpy determinations are summarized in table 2. Since the heat capacities are listed in chronological sequence, the temperature increments employed in the determinations may usually be inferred from the temperature differences between adjacent determinations. The results are shown together with some earlier low-temperature results in figure 1, while earlier results at higher temperatures are incorporated in figure 2.

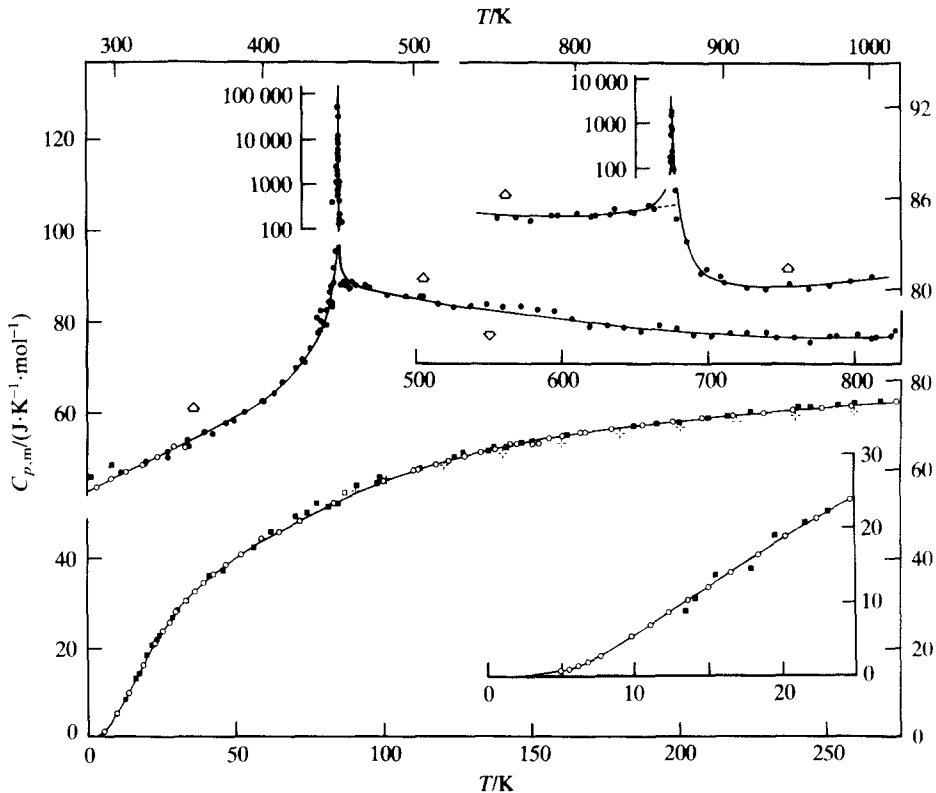


FIGURE 1. Heat capacity of Ag<sub>2</sub>S. ○, Present results U of M; ●, Present results, U of O; +, Gulyaev and Petrov;<sup>(1)</sup> ■, Walsh *et al.*<sup>(2)</sup>

TABLE 1. Heat capacity of silver(I) sulfide, Ag<sub>2</sub>S, and of Ag<sub>2.0526</sub>S

$\langle T \rangle$ K	$C_{p,m}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\langle T \rangle$ K	$C_{p,m}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\langle T \rangle$ K	$C_{p,m}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\langle T \rangle$ K	$C_{p,m}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
University of Michigan		$M(\text{Ag}_2\text{S}) = 247.80 \text{ g} \cdot \text{mol}^{-1}$					
Series I		187.25	69.099	13.642	9.958	82.625	52.103
145.66	64.848	197.78	69.894	14.997	11.845	89.886	53.329
150.29	64.823	208.19	70.592	16.553	13.870	99.207	56.890
155.69	66.078	218.50	71.274	18.345	16.180	110.69	59.132
161.02	66.659	228.75	71.843	20.289	18.506	121.59	61.191
166.29	67.182	238.91	72.408	22.414	20.841	132.37	63.024
144.72	64.743	248.98	72.952	24.672	23.414	143.20	64.567
152.43	64.865	258.98	73.438	27.049	25.573	$\Delta H$ Detn. A	
160.18	66.551	273.91	74.166	29.591	27.769	$\Delta H$ Detn. B	
168.04	67.392			33.031	30.476	276.19	74.203
Series III				35.830	32.401	285.82	74.793
Series II		4.951	0.724	38.898	34.275	295.71	75.212
109.71	58.969	5.457	0.971	42.305	36.116	306.02	75.659
117.48	60.471	6.151	1.431	46.468	38.204	316.35	76.111
127.11	62.174	6.867	1.946	51.437	40.413	326.71	76.626
137.15	63.710	7.709	2.711	56.787	42.555	337.42	77.312
147.45	65.065	8.699	3.728	58.282	44.011	346.18	77.224
155.84	66.082	9.895	5.146	64.671	45.526		
165.79	67.166	11.155	6.619	71.270	47.760		
176.60	68.191	12.378	8.205	75.032	49.020		
University of Oslo		Series IV					
Series I		303.26	75.63	444.37	87.09	Series X	
319.94	76.41	318.40	76.23	$\Delta H$ Detn. I		788.18	84.66
333.23	76.98	333.58	76.59	Series VIII		801.11	84.78
346.46	77.73	348.72	77.34	$\Delta H$ Detn. J		814.08	84.60
359.63	78.36	363.81	78.09	444.25	86.88	827.07	85.08
372.74	78.87	378.85	78.96	$\Delta H$ Detn. K		840.04	84.78
385.81	79.56	390.33	79.98	453.27	88.20	853.03	85.08
398.84	80.28	405.30	80.88	456.85	88.02	$\Delta H$ Detn. K	
411.81	81.66	420.13	82.53	460.42	88.23	875.67	82.98
424.72	83.10	434.94	84.96	467.00	88.25	888.96	81.12
437.53	85.77	444.15	86.76	Series IX		902.39	80.43
$\Delta H$ Detn. C		$\Delta H$ Detn. F		504.26	87.36	915.92	79.86
481.05	87.55	456.02	88.08	515.53	86.85	929.58	79.74
493.88	87.42	459.72	87.69	526.88	86.64	945.22	80.22
506.75	87.36	Series V		538.08	86.70	959.00	79.77
Series II		430.07	83.91	549.52	86.82	972.85	79.98
427.62	82.92	439.20	85.44	561.01	86.66	986.81	80.31
434.06	85.81	442.83	85.83	572.54	86.61	1000.90	80.58
440.44	87.12	446.46	87.33	584.13	86.40	Series XI	
$\Delta H$ Detn. D		$\Delta H$ Detn. G		595.76	86.31	810.90	84.54
457.45	88.32	455.13	88.38	607.48	85.86	823.84	84.69
Series III		Series VI		619.28	85.35	836.66	84.90
441.24	85.41	436.37	85.11	631.13	85.50	$\Delta H$ Detn. L	
442.68	86.04	443.64	86.73	643.05	85.26	885.25	80.82
444.11	87.00	$\Delta H$ Detn. H		655.06	84.99	899.02	80.67
445.52	89.28	455.25	87.42	666.59	85.32	$\Delta H$ Detn. M	
446.94	90.51	458.89	87.99	678.68	85.20	$\Delta H$ Detn. N	
$\Delta H$ Detn. E		Series VII		690.87	84.75	Series XII	
450.92	88.32	$\Delta H$ Detn. E		703.12	84.69	747.00	84.54
452.32	88.44	437.46	85.38	715.43	84.90	759.24	84.51
453.72	88.23			727.80	84.84	771.54	84.24
				740.23	84.84	783.88	84.69

TABLE 1—continued

$\langle T \rangle$ K	$C_{p,m}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\langle T \rangle$ K	$C_{p,m}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\langle T \rangle$ K	$C_{p,m}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\langle T \rangle$ K	$C_{p,m}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
University of Oslo							
$M(\text{Ag}_2\text{S}_{1.0526}) = 249.48 \text{ g} \cdot \text{mol}^{-1}$							
Series I		554.43	88.61	634.52	87.03	458.74	91.58
467.22	90.76	565.56	88.24	646.30	86.54	462.55	90.26
477.95	90.22					466.37	90.38
488.72	90.21	Series II		Series III		Series IV <sup>a</sup>	
499.54	89.96	576.92	87.65	424.30	85.13		
510.40	89.65	588.19	86.88	435.73	86.86	384.76	79.44
521.32	89.22	599.40	87.08	443.35	87.51	388.49	102.8 <sup>b</sup>
532.30	88.90	611.04	86.75	$\Delta H$ Detn. O		392.22	80.08
543.34	88.68	622.78	87.11	454.94	90.88		

<sup>a</sup> Heat capacities adjusted for the presence of 0.047 mol of S, but not for its enthalpy of fusion.

<sup>b</sup>  $\Delta T = 3.5255 \text{ K}$ ;  $\Delta_{\text{trs}}H/\Delta_{\text{fus}}H_m = 81.3 \text{ J}/1717 \text{ J} \cdot \text{mol}^{-1} \hat{=} 0.0474 \text{ mol}$  of S.

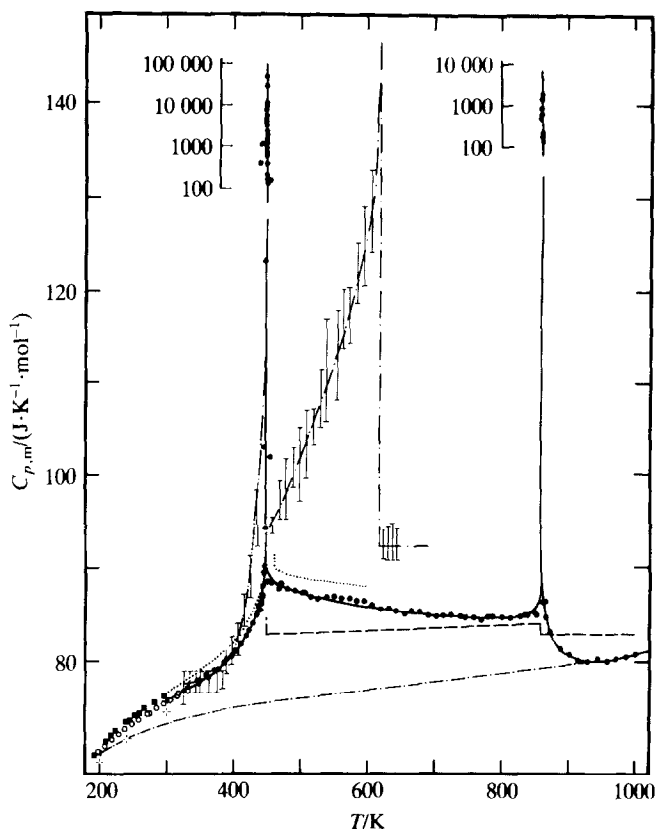


FIGURE 2. Heat capacity of Ag<sub>2</sub>S. ○, Present results U of M; ●, present results U of O; +, Gulyaev and Petrov;<sup>(1)</sup> ■, Walsh *et al.*;<sup>(2)</sup> ···, Jost and Kubaschewski;<sup>(3)</sup> ●—●, Perrott and Fletcher<sup>(4)</sup> with spread indicated by I; ---, Thompson and Flengas;<sup>(30)</sup> ····, estimated non-translational lattice heat capacity at constant pressure.

TABLE 2. Fractional enthalpies of transition

$\langle T \rangle$ K	$\Delta T$ K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	$C_{p,m(n.t.)}$ $J \cdot K^{-1} \cdot mol^{-1}$	$\Delta t_{stab}$ min	$\Delta H_{m.exc}$ $J \cdot mol^{-1}$	$T_{final}$ K
$M(Ag_2S) = 247.80 \text{ g} \cdot mol^{-1}$						
$\alpha$ -to- $\beta$ transition of $Ag_2S$						
$\Delta H$ Detn. C						
446.609	5.418	361.2	87.4	80	1483	449.318
449.745	0.855	2917	88.0	65	2418	450.173
456.068	11.790	101.9	88.2	64	162	461.963
					4063	
$\Delta H$ Detn. D						
446.215	5.201	123.2	87.3	259	186	448.816
449.100	0.568	2111	88.0	164	1149	449.384
449.417	0.066	38050	88.1	416	2505	449.450
451.872	4.844	138.7	88.3	343	244	450.294
					4084	
$\Delta H$ Detn. E						
448.246	1.2028	126.9	87.8	48	47	448.847
449.052	0.4100	635	87.9	156	224	449.257
449.271	0.0280	10870	88.0	158	302	449.285
449.300	0.0285	10700	88.0	158	302	449.314
449.332	0.0363	8337	88.0	149	299	449.350
449.366	0.0311	9927	88.0	301	306	449.381
449.400	0.0371	8085	88.0	158	297	449.418
449.443	0.0503	6018	88.0	159	298	449.469
449.493	0.0492	6162	88.0	163	299	449.518
449.552	0.0674	4464	88.1	81	295	449.585
449.602	0.0327	9273	88.1	165	300	449.618
449.633	0.0296	9645	88.1	73	283	449.648
449.672	0.0487	6180	88.1	166	297	449.696
449.717	0.0793	3723	88.1	209	288	449.775
449.991	0.4314	582.3	88.2	120	213	450.207
					4050	
$\Delta H$ Detn. F						
447.548	3.108	126.1	87.6	66	120	449.102
449.328	0.453	1932	88.0	1156	835	449.554
449.929	0.750	919	88.2	163	623	450.304
450.530	0.453	1583	88.3	120	677	450.757
450.775	0.036	26140	88.4	1255	938	450.793
450.983	0.381	1935	88.4	181	704	451.174
452.673	2.999	140.9	88.4	58	157	453.173
					4054	
$\Delta H$ Detn. G						
448.697	0.869	674.3	87.9	1136	510	449.132
449.236	0.208	3411	88.0	130	691	449.340
449.643	0.606	4770	88.1	156	2837	449.946
451.650	3.408	96.95	88.35	319	29	453.354
					4067	



TABLE 2—continued

$\langle T \rangle$ K	$\Delta T$ K	$C_{p,m}$ J · K <sup>-1</sup> · mol <sup>-1</sup>	$C_{p,m}(n.t.)$ J · K <sup>-1</sup> · mol <sup>-1</sup>	$\Delta t_{stab}$ min	$\Delta H_{m,exc}$ J · mol <sup>-1</sup>	$T_{final}$ K
$\Delta H$ Detn. H						
448.354	2.152	1266	87.8	128	2535	449.430
449.472	0.084	8865	88.0	157	737	449.514
449.711	0.395	1970	88.1	936	743	449.909
451.666	3.514	94.47	88.35	55	22	453.423
					4037	
$\Delta H$ Detn. I						
448.354	1.829	1505	87.8	107	2592	449.490
449.570	0.160	4635	88.1	148	728	449.650
450.314	1.330	629.4	88.3	42	720	450.979
					4040	
$\Delta H$ Detn. J						
447.485	2.866	149.6	87.6	38	149	448.918
449.139	0.438	1571	88.0	175	650	449.355
449.541	0.363	3966	88.1	130	1408	449.718
449.950	0.454	3150	88.2	68	1390	450.172
450.825	1.307	448.2	88.4	85	470	451.479
					4067	
				$\Delta_{irs} H_m$ :	4058 ± 26	
$\beta$ -to- $\gamma$ transition of Ag <sub>2</sub> S						
$\Delta H$ Detn. K						
853.035	12.9983	85.08	84.98	41	4	859.534
864.302	9.5351	166.0	84.8	49	774	869.069
					778	
$\Delta H$ Detn. L						
849.417	12.7796	85.38	84.96	73	8	855.807
860.527	9.4412	165.6	85.0	73	761	865.248
871.828	13.1591	85.00	83.45	67	20	878.407
					789	
$\Delta H$ Detn. M						
863.127	1.9372	159.1	85.0	27	144	864.096
864.184	0.1764	1662	85.0	37	278	864.273
864.431	0.3173	863	85.0	71	247	864.590
865.081	0.9815	186.1	85.0	33	99	865.572
866.219	1.2949	93.15	84.65	53	11	866.867
867.555	1.3774	86.37	84.40	33	3	868.244
868.917	1.3474	84.72	84.00	54	1	869.591
					783	
$\Delta H$ Detn. N						
858.888	9.3285	91.68	84.98	32	63	863.552
863.819	0.5331	450.6	85.0	39	195	864.086
864.171	0.1725	1525	85.0	36	248	864.258
864.477	0.4386	551.7	85.0	44	205	864.696
865.248	1.1035	142.8	85.0	35	64	865.800
866.481	1.3619	93.72	84.55	29	12	867.162
867.874	1.4222	84.42	84.5	26	0	868.584
					787	
				$\Delta_{irs} H_m$ :	784 ± 5	

TABLE 2—continued

$\langle T \rangle$ K	$\Delta T$ K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	$C_{p,m(n.t.)}$ $J \cdot K^{-1} \cdot mol^{-1}$	$\Delta t_{stab}$ min	$\Delta H_{m,exc}$ $J \cdot mol^{-1}$	$T_{final}$ K
$M(Ag_2S_{1.005}) = 247.96 \text{ g} \cdot mol^{-1}$						
$\alpha$ -to- $\beta$ transition in $Ag_2S_{1.0526}$ sample with sulfur excess subtracted						
$\Delta H$ Detn. O						
447.126	3.7529	89.88	87.5	44	9	449.004
450.068	2.1129	256.5	88.2	52	356	451.117
451.132	0.029	56128	88.4	204	1625	451.146
451.174	0.056	14538	88.4	128	809	451.202
451.241	0.078	10408	88.4	131	805	451.280
452.164	1.7668	332.4	88.4	45	431	453.047
$\Delta_{trs}H_m:$					4035	

The estimated standard deviation of a single measurement in the low-temperature determinations is about 5 per cent at 10 K and 0.08 per cent over the region 30 to 350 K. The corresponding value for the high-temperature determinations is 0.25 per cent. The experimental heat capacities for the low- and high-temperature regions were fitted to polynomials in temperature by the method of least squares. The fitting and especially the joins between fitted segments were checked by inspection of a plot of  $dC_p/dT$  against  $T$ . At the lowest temperatures the heat capacities were smoothed with the aid of a plot of  $C_p/T$  against  $T^2$  and the thermodynamic functions extrapolated by this linear relation. From this plot the electronic heat-capacity coefficient was found to be zero within the experimental error limits.

To evaluate and compare the different determinations through the transition regions (compare table 2) non-transitional—or rather reference—heat capacities had to be derived. For this purpose the least-squares-fitted polynomial expressions for the heat capacity of  $\beta$ - $Ag_2S$  were extrapolated to give  $88.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at 451.3 and  $85.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at 865.0 K. In the  $\alpha$ - $Ag_2S$  region the heat capacity was extrapolated linearly from  $87.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at 445 K to the same value as for  $\beta$ - $Ag_2S$  at 451.3 K. Considerable pre- and post-transitional contributions which are not included in the results of table 2 will be considered later.

Smoothed values of the heat capacity  $C_{p,m}$ , entropy  $\{S_m^\circ(T) - S_m^\circ(0)\}$ , enthalpy  $\{H_m^\circ(T) - H_m^\circ(0)\}$ , and the function  $-\{[G_m^\circ(T) - H_m^\circ(0)]/T\}$  are given for selected temperatures in table 3. Up to 350 K the heat capacity is judged to be precise within  $\pm 0.2$  per cent and the other thermodynamic functions within  $\pm 0.15$  per cent, values which correspond to twice the standard deviation in the results. In the higher-temperature region the corresponding precision indices are 0.4 and 0.3 per cent, respectively.

#### 4. Discussion

The present heat-capacity results are about 1 per cent lower than those by Walsh *et al.*<sup>(2)</sup> in the 250 to 300 K region while the differences become more erratic in the

TABLE 3. Thermodynamic properties of silver(I) sulfide.  
 $M(\text{Ag}_2\text{S}) = 247.80 \text{ g} \cdot \text{mol}^{-1}$ 

$T$ K	$C_{p,m}$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$S_m^\circ(T) - S_m^\circ(0)$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$H_m^\circ(T) - H_m^\circ(0)$ $\text{J} \cdot \text{mol}^{-1}$	$-\{G_m^\circ(T) - H_m^\circ(0)\}_T / T$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
0	0	0	0	0
5	0.745	0.167	0.626	0.041
10	5.216	1.842	13.982	0.444
15	11.795	5.178	56.24	1.429
20	18.18	9.466	131.52	2.890
25	23.63	14.127	236.46	4.668
30	28.14	18.85	366.23	6.638
40	34.89	27.93	683.6	10.840
50	39.75	36.26	1057.8	15.10
60	43.81	43.87	1476.0	19.27
70	47.50	50.91	1932.8	23.30
80	50.90	57.48	2425.0	27.16
90	53.99	63.65	2949.8	30.88
100	56.72	69.49	3503.7	34.45
120	61.05	80.23	4683.8	41.20
140	64.14	89.89	5937	47.48
160	66.50	98.61	7245	53.33
180	68.46	106.56	8595	58.81
200	70.11	113.86	9981	63.96
220	71.43	120.61	11397	68.80
240	72.47	126.87	12836	73.39
260	73.42	132.71	14295	77.73
280	74.44	138.18	15773	81.85
298.15	75.31	142.89	17132	85.43
300	75.39	143.35	17271	85.78
320	76.32	148.24	18789	89.53
350	77.66	155.14	21098	94.86
400	80.47	165.67	25044	103.07
450	(88.11) <sup>a</sup>	(175.52)	(29225)	(110.57)
451.30	(88.40)	(175.77)	(29339)	(110.76)
$\alpha\text{-Ag}_2\text{S}$ to $\beta\text{-Ag}_2\text{S}$ transition				
451.30	(88.40)	(184.80)	(33397)	110.80
500	87.26	193.79	37670	118.45
550	86.65	202.08	42017	125.68
600	86.03	209.59	46335	132.37
850	85.35	216.45	50620	138.57
700	84.80	222.75	54872	144.37
750	84.56	228.59	59104	149.79
800	84.69	234.05	63334	154.89
850	84.97	239.20	67576	159.70
865.00	(85.00)	(240.68)	(68852)	(161.09)
$\beta\text{-Ag}_2\text{S}$ to $\gamma\text{-Ag}_2\text{S}$ transition				
865.00	(85.00)	(241.59)	(69636)	161.09
900	80.38	244.84	72506	164.28
950	79.91	249.17	76506	168.64
1000	80.57	253.28	80512	172.77

<sup>a</sup> The values in parentheses are predicated on the assumption that the transition is isothermal.

TABLE 4. Enthalpies of transitions of silver(I) sulfide.  
 $M(\text{Ag}_2\text{S}) = 247.80 \text{ g} \cdot \text{mol}^{-1}$ 

$\frac{T_{\text{trs}}}{\text{K}}$	$\frac{\Delta_{\text{trs}}H_m}{\text{kJ} \cdot \text{mol}^{-1}}$	Method	Authors	Year
$\alpha\text{-Ag}_2\text{S}$ to $\beta\text{-Ag}_2\text{S}$				
448	$3.98 \pm 0.04$	Bunsen-type ice-calorimeter	Bellati and Lussana <sup>(29)</sup>	1889
452	$4.39 \pm 0.08$	Metal block	Kapustinskii and Veselovskii <sup>(28)</sup>	1938
449	$6.38 \pm 1.76$	Clapeyron	Roy <i>et al.</i> <sup>(31)</sup>	1959
450	$3.98^a \pm 0.42$	$C_p$	Perrott and Fletcher <sup>(4)</sup>	1969
450	$6.49^b \pm 0.42$	$C_p$	Perrott and Fletcher <sup>(4)</sup>	1969
449	$3.93 \pm 0.20$	Drop calorimeter	Thompson and Flengas <sup>(30)</sup>	1971
441 to 453	$4.37 \pm ?$	d.t.a.	Mamedov <i>et al.</i> <sup>(32)</sup>	1980
449.3 to 451.3	$4.06 \pm 0.03$	Adiabatic $C_p$	This work	
$\beta\text{-Ag}_2\text{S}$ to $\gamma\text{-Ag}_2\text{S}$				
859	$0.50 \pm 0.54$	Drop calorimeter	Thompson and Flengas <sup>(30)</sup>	1971
865	$0.784 \pm 0.005$	Adiabatic $C_p$	This work	

<sup>a</sup> Stoichiometric sample.<sup>b</sup> Non-stoichiometric samples.

lower-temperature range. The results by Gulyaev and Petrov<sup>(1)</sup> were again about 2 per cent lower than the present values in the 200 to 300 K region and showed a rather large spread. The good correspondence between the values of Walsh *et al.*<sup>(2)</sup> and of Jost and Kubaschewski<sup>(3)</sup> over the common region made us recheck the composition of our sample by determination of its silver content (see section 2). It corresponded to the sample composition  $\text{Ag}_{2.003}\text{S}$ , which we consider to represent exact stoichiometry within the limit of error of the analysis. The derived standard entropy:  $S_m^\circ(298.15 \text{ K}) = (142.89 \pm 0.44) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , is 0.4 per cent lower than that found by Walsh *et al.*<sup>(2)</sup> and 1.3 per cent higher than that obtained by Mills<sup>(24)</sup> by integration of the results by Gulyaev and Petrov.<sup>(1)</sup> Electrochemical-cell results by Goates *et al.*,<sup>(25)</sup> Kimura,<sup>(26)</sup> and Kiukkola and Wagner<sup>(27)</sup> were also evaluated by Mills,<sup>(24)</sup> who selected the value  $S_m^\circ(298.15 \text{ K}) = (143.5 \pm 1.2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

The present heat-capacity results are systematically about 1 per cent lower than those shown in the plot by Jost and Kubaschewski<sup>(3)</sup> until the  $\alpha$ -to- $\beta$  transition is approached. This is true also for the decreasing heat capacity in the  $\beta\text{-Ag}_2\text{S}$  region up to 620 K. Kapustinskii and Veselovskii<sup>(28)</sup> reported a much higher average heat capacity ( $92.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ) over the range 452 to 843 K, as did Bellati and Lussana<sup>(29)</sup> over the range 452 to 594 K. The enthalpy equation derived by Thompson and Flengas<sup>(30)</sup> from their drop-calorimetric experiments indicated a much lower and slightly rising heat capacity ( $82.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at 450 K to  $83.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at 860 K). These determinations and earlier ones referred to by Kapustinskii and Veselovskii<sup>(28)</sup> are considered as superseded by the present results. It is remarkable, however, that the enthalpy results by Thompson and Flengas,<sup>(30)</sup> which agree so well with the present results to just above the  $\alpha$ -to- $\beta$  transition, become about  $1 \text{ kJ} \cdot \text{mol}^{-1}$  lower both at 850 and 1000 K.

No enthalpy of transition was given by Jost and Kubaschewski.<sup>(3)</sup> Results

obtained by other investigators are given in table 4. The values by Bellati and Lussana,<sup>(29)</sup> Thompson and Flengas,<sup>(30)</sup> Kapustinskii and Veselovski,<sup>(28)</sup> and Mamedov *et al.*<sup>(32)</sup> agree reasonably well with the present one. That by Roy *et al.*<sup>(31)</sup> and those by Perrott and Fletcher<sup>(4)</sup> for their non-stoichiometric samples exceed the present value by more than 50 per cent. Application of the Clapeyron equation, using the more recent  $(dT/dp)_{\alpha+\beta}$  value  $16 \times 10^{-9} \text{ K} \cdot \text{Pa}^{-1}$  by Clark and Rapoport<sup>(33)</sup> together with  $\Delta_{\text{trs}} V_m = 0.16 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$  by Kimura,<sup>(26)</sup> leads to  $\Delta_{\text{trs}} H_m = (4.5 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$ . The apparently closely corresponding transitional enthalpy increment for the stoichiometric  $\text{Ag}_2\text{S}$  of Perrott and Fletcher<sup>(4)</sup> is, however, hardly comparable as it is followed by another one amounting to  $(2.50 \pm 0.42) \text{ kJ} \cdot \text{mol}^{-1}$  in a region where we find no transition.

Since there was no sign of the extra transition reported by Perrott and Fletcher<sup>(4)</sup> for stoichiometric  $\text{Ag}_2\text{S}$ , we decided to change the composition of our sample to see how excess sulfur affects its thermodynamic behavior. Heat-capacity measurements on a sample with overall composition  $\text{Ag}_2\text{S}_{1.0526}$  were first performed in the 450 to 650 K range. The observed values decreased from about  $91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at the former temperature to about  $86.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at the latter. This decrease is somewhat steeper than for the stoichiometric sample. The 2.5 to  $1.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  higher heat-capacity values are in reasonable agreement with the presence of about 0.05 mol of S in the sample, in view of the pronounced heat-capacity changes which occur in liquid sulfur in this temperature range and also the increasing solubility of sulfur in  $\text{Ag}_2\text{S}$  with temperature.

One evaluation of the  $\alpha$ -to- $\beta$  transition enthalpy, see table 2, gave  $\Delta_{\text{trs}} H_m = 4035 \text{ J} \cdot \text{mol}^{-1}$ , within the range of uncertainty for the stoichiometric compound. The sample was then cooled overnight to about 370 K before the excess sulfur in it was determined from its enthalpy of fusion:  $\Delta_{\text{fus}} H_m = 1717 \text{ J} \cdot \text{mol}^{-1}$  for S according to West.<sup>(34)</sup> The enthalpy increment corresponded to the presence of 0.047 mol of S and thus to the composition  $\text{Ag}_2\text{S}_{1.005}$  for the coexisting  $\alpha$ - $\text{Ag}_2\text{S}$ . Whether this apparent sulfur excess is real or possibly caused by impurities remains to be investigated.

The extra transition reported by Perrott and Fletcher<sup>(4)</sup> was not observed, but it might possibly be associated with the presence of another phase. Thus, Jeannot<sup>(35)</sup> reported the compound  $\text{Ag}_4\text{S}$  and found that it decomposed—presumably into  $(\text{Ag} + \text{Ag}_2\text{S})$ —in vacuum ( $\approx 1 \text{ Pa}$ ) at  $(587 \pm 20) \text{ K}$ .

The fractional enthalpy determinations of the  $\alpha$ -to- $\beta$  transition show that it does not occur at a well-defined temperature, but covers a variable range depending upon the previous history of the sample. In the three first series of determinations (C, D, and E), the measurements were begun without any extended equilibration below the  $\alpha$ -to- $\beta$  transition temperature, and under these conditions the transition is practically complete at  $(450.1 \pm 0.1) \text{ K}$ . Afterwards the sample was tempered at 420 K for 2 a and the low-temperature measurements were then completed. In the next determination through the transition region (F), the transition is only about 1/3 completed at 450.3 K; and it extends to above 451.2 K. Repeated measurements without extended tempering of the sample indicate practical completion of the transition at 450.0 K (G, H, and I). The sample was finally tempered for 14 d at

420 K and the last series of runs in the transition region (J) again show an extension of the transition to higher temperatures, but not as pronounced as that after 2 a of tempering.

The slowness of the transition is in keeping with the results by Bonnacaze *et al.*<sup>(36)</sup> who found that about 150 d of tempering below 450 K were needed to obtain stable coulometric titrations, *i.e.* a very long time compared with the relaxation time for point defects in  $\alpha$ -Ag<sub>2</sub>S. It resulted in a decrease in width of the homogeneity range by a factor of about 10 from the results by Valverde<sup>(37)</sup> at 420 K. The results by Bonnacaze *et al.*<sup>(36)</sup> were largely confirmed by Reye and Schmalzried<sup>(38)</sup> on  $\alpha$ -Ag<sub>2+ $\delta$</sub> S crystals prepared below the transition temperature and lead to a homogeneity range with  $\Delta\delta$  of about  $1 \times 10^{-5}$  at 440 K. The behavior was found to be in accordance with ideal point-defect thermodynamics.

Just above the transition temperature a 1000-fold widening of the homogeneity range occurs, and this is towards increasing silver content only. Wagner<sup>(39)</sup> in his pioneering study found the limits to be Ag<sub>2.002</sub>S and close to Ag<sub>2.000</sub>S at 470 K. Later calculations and experimental results (see Schmalzried and Reye)<sup>(8)</sup> place the silver-rich limit at Ag<sub>2.0020</sub>S and the sulfur-rich limit at Ag<sub>2.0002</sub>S at 450 K. The resulting phase relations are shown in figure 3.

The interval melting observed for stoichiometric Ag<sub>2</sub>S in the present study might

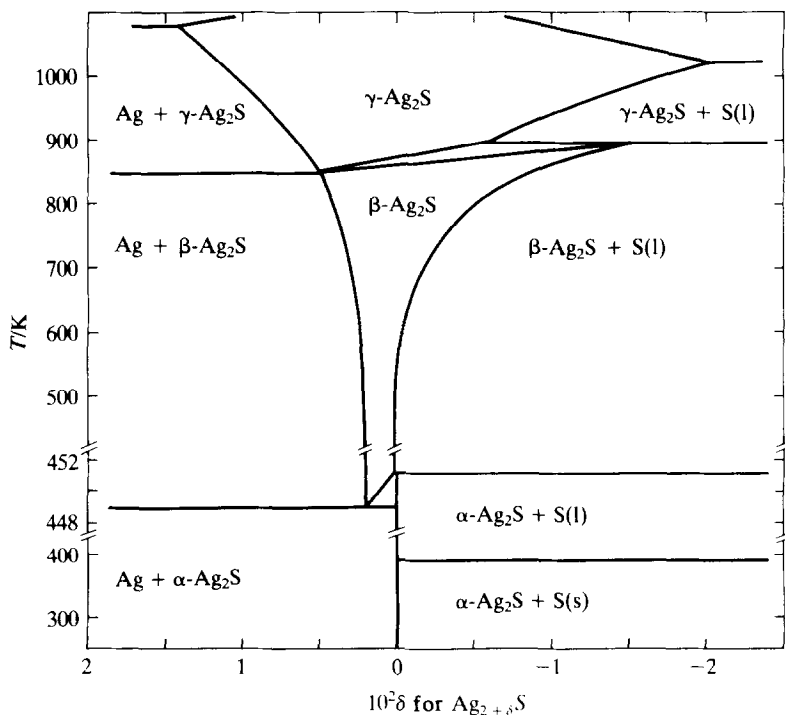


FIGURE 3. (Silver + sulfur) phase diagram in the composition range  $\text{Ag}_{2+\delta}\text{S}$ , where  $0.020 > \delta > -0.025$ . Phase boundaries at saturation pressures are mainly results of the calculations by Rau.<sup>(9)</sup>

thus arise from a very slight silver excess ( $\delta \approx +0.0002$ ), and the continuous and broad transition of the fully transformed sample (see table 2, Detn. E) support this view. Incomplete equilibration below 450 K might lead to the formation of a (slightly non-stoichiometric?)  $\alpha'$ -Ag<sub>2</sub>S phase, which reverts back to  $\beta$ -Ag<sub>2</sub>S on heating to about 449.3 K. The presence of such an intermediate metastable phase has been reported by Mamedov *et al.*<sup>(32)</sup> and Boettcher *et al.*<sup>(40)</sup> In either case, on tempering below the transition temperature the  $\beta$ - or  $\alpha'$ -Ag<sub>2</sub>S slowly converts to the stable stoichiometric  $\alpha$ -Ag<sub>2</sub>S phase with a slightly higher transition temperature. Sulfur excess (see table 2, Detn. O) is seen to largely prevent non-isothermal transition behavior, even after a short equilibration time, and the major part of the transitional enthalpy is taken up between 451.0 and 451.3 K.

The presence of a further solid-state transition in Ag<sub>2</sub>S was reported by Urazova.<sup>(41)</sup> A change in transition temperature from 849 K on the silver-rich side to 865 K on the sulfur-rich side was related to a variable composition of the  $\beta$ - and  $\gamma$ -Ag<sub>2</sub>S phases from 12.52 to 13.07 mass per cent of sulfur, *i.e.* from Ag<sub>2.077</sub>S to Ag<sub>1.977</sub>S. Somewhat different results were obtained by Kracek,<sup>(5)</sup> who gave the composition range as Ag<sub>2.04</sub>S to Ag<sub>1.88</sub>S with transition temperature increasing from 859 to 894 K. A much narrower composition range was inferred by Rau<sup>(9)</sup> from sulfur-fugacity measurements on Ag<sub>2+ $\delta$</sub> S and defect-model calculations. The resulting phase boundaries are indicated in figure 3. A calorimetric determination of the small enthalpy change associated with the transition was made by Thompson and Flengas,<sup>(30)</sup> but the uncertainty was as large as the observed value, see table 4. In the present work the transition appeared well-behaved and reproducible but was not sharp. The enthalpy and entropy of transition are  $\Delta_{\text{trs}}H_m = (784 \pm 6) \text{ J} \cdot \text{mol}^{-1}$  and  $\Delta_{\text{trs}}S_m = (0.907 \pm 0.003) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . The transition occurs in the range 863 to 866 K and calls for a narrower ( $\beta + \gamma$ )-Ag<sub>2</sub>S diphasic range at the stoichiometric composition than is indicated in figure 3. Possibly, the transition is continuous and does not involve a two-phase region.

In the  $\gamma$ -Ag<sub>2</sub>S region the heat capacity decreases to a minimum of about  $80 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at 950 K. It then rises again as the melting temperature is approached:  $T_m = (1109 \pm 6) \text{ K}$ .<sup>(5, 30, 42, 43)</sup> The drop-calorimetric results by Thompson and Flengas<sup>(30)</sup> also led to a lower heat capacity for  $\gamma$ -Ag<sub>2</sub>S than for  $\beta$ -Ag<sub>2</sub>S, but not as low as found here. In fact, the subtraction of a normal dilational heat-capacity contribution in the 900 to 1000 K range results in a constant-volume heat capacity for  $\gamma$ -Ag<sub>2</sub>S considerably below the classical limit.

The non-transitional heat capacity of the Ag<sub>2</sub>S phases, which form the basis for the derived enthalpies and entropies of transition in table 4, was chosen on the assumption that the transitions were almost isothermal. This assumption is clearly unwarranted, as evidenced by the high heat-capacity values at considerable distances from the temperature of the maximum. Constant-volume lattice heat-capacity values  $C_{v,m}(l)$ , which take the grossly anharmonic vibrations of the silver atoms into account, have not yet been derived. Approximate values for  $C_{v,m}(l)$  can be obtained by applying the Nernst-Lindemann relation outside the transition regions:

$$C_m(d) = C_{p,m} - C_{v,m} = AC_{p,m}^2(T/T_m),$$

where  $C_m(d)$  is the dilational heat capacity,  $A = 0.00171 \text{ J}^{-1} \cdot \text{K} \cdot \text{mol}$  for 3 atoms, and  $T_m$  the melting temperature: 1109 K. At 1000 K then,  $C_{v,m} = 70.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  or 94.3 per cent of the value in the harmonic approximation. Application of the Nernst–Lindemann relation to the heat capacity of  $\alpha\text{-Ag}_2\text{S}$  in the 100 to 200 K region, in combination with the Debye heat-capacity model, leads to a maximum  $\Theta_D = 258 \text{ K}$  at 160 K. This Debye temperature is used for calculating the harmonic  $C_{v,m}(l)$  in the higher-temperature region. Anharmonicity contributions are subtracted for  $\beta$ - and  $\gamma\text{-Ag}_2\text{S}$  on the rough assumption of proportionality with  $T$ . Addition of the Nernst–Lindemann dilation contribution then leads to the non-transitional  $C_{p,m}$  values shown in figure 2 and to the  $\Delta_{\text{trs}} C_{p,m}$  values shown in figure 4.

The dilational heat capacity can also be calculated using the thermodynamic relation:

$$C_m(d) = (\alpha^2/\kappa)V_m T,$$

where  $\alpha$  is the isobaric expansivity,  $\kappa$  the isothermal compressibility, and  $V_m$  the molar volume. Room-temperature experimental values are:  $\alpha = 39 \times 10^{-6} \text{ K}^{-1}$  (303 to 348 K);<sup>(44)</sup>  $45.6 \times 10^{-6} \text{ K}^{-1}$  (300 to 448 K);<sup>(45)</sup>  $126 \times 10^{-6} \text{ K}^{-1}$  (293 to 393 K);<sup>(32)</sup>  $140 \times 10^{-6} \text{ K}^{-1}$  (303 to 363 K);<sup>(46)</sup>  $\kappa = 32 \times 10^{-12} \text{ Pa}^{-1}$ ,<sup>(44)</sup>  $120 \times 10^{-12} \text{ Pa}^{-1}$ ,<sup>(47)</sup>  $V_m = 34.3 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ .<sup>(46)</sup> More definite values for expansivity and compressibility are needed in order to derive a useful value in this way. By way of its general nature the expression also includes the transitional

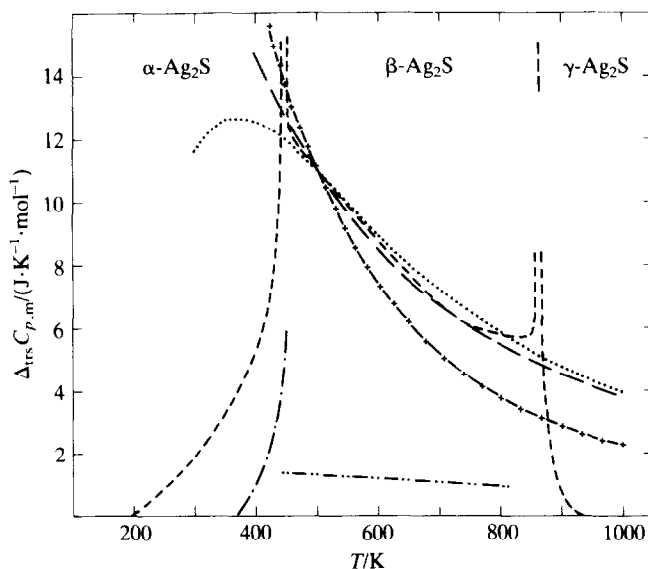


FIGURE 4. Estimated transitional heat capacities for  $\text{Ag}_2\text{S}$ . — — —, Present results; ····, results below 450 K by Jost and Kubaschewski;<sup>(3)</sup> ····, estimate above 450 K by Schmalzried;<sup>(18)</sup> — — —, calculated curve for  $\beta\text{-Ag}_2\text{S}$ , fitted to the Schmalzried<sup>(18)</sup> equation at 500 K; ····, calculated Schottky heat capacity for  $2\text{Ag}$  with  $g_0/g_1 = 1/2$  and  $\Delta E/hc = 685 \text{ cm}^{-1}$ ; + + +, calculated Schottky heat capacity for  $g_0/g_1 = 1/5.74$  and  $\Delta E/hc = 570 \text{ cm}^{-1}$ .



component of the dilation contribution and might thus be larger than the Nernst–Lindemann value derived in the previous paragraph.

Around 550 K the isobaric expansivity for  $\beta$ -Ag<sub>2</sub>S is  $113 \times 10^{-6} \text{ K}^{-1}$  (458 to 558 K) according to Lehovc<sup>(45)</sup> and about  $90 \times 10^{-6} \text{ K}^{-1}$  according to Glazov and Makhdumova.<sup>(46)</sup> The four lattice-constant determinations by Cava *et al.*<sup>(13)</sup> in the range 459 to 598 K lead to  $\alpha = 115 \times 10^{-6} \text{ K}^{-1}$ , while the three determinations by Djurle<sup>(14)</sup> in the range 462 to 773 K indicate a somewhat lower value:  $\alpha = 75 \times 10^{-6} \text{ K}^{-1}$ . Thus, the experimental expansivities around 550 K are consistently about  $110 \times 10^{-6} \text{ K}^{-1}$ . The compressibility of  $\beta$ -Ag<sub>2</sub>S is unknown, however, and Schmalzried<sup>(18)</sup> used  $\kappa = 50 \times 10^{-12} \text{ Pa}^{-1}$  at 450 K in his calculations. The resulting dilation contribution is then  $9.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , or about twice as high as the Nernst–Lindemann estimate used here. It would thus diminish the transitional heat capacity in figure 4 to about  $5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at 550 K, but this value is still four times larger than that used in the calculations by Schmalzried.<sup>(18)</sup>

The earlier transitional heat-capacity estimate for  $\alpha$ -Ag<sub>2</sub>S by Jost and Kubaschewski<sup>(3)</sup> was apparently a result of extrapolation of the practically linearly rising total heat capacity in the range 250 to 380 K and of using it as the lattice heat capacity at constant pressure. The excess heat capacity was analyzed in terms of Frenkel defects among the silver cations by the expression derived earlier by Jost:<sup>(48)</sup>

$$\Delta C_{p,m} T^2 = \{\exp(\Delta S_m/2R)\}(\Delta H_m^2/2R)\exp(-\Delta H_m/2RT),$$

by plotting  $\log(\Delta C_{p,m} T^2)$  against  $1/T$ , see figure 5. Our choice of lattice heat capacity at constant pressure does not lead to a strictly linear relation, but such an approximation over the range 300 to 430 K gives  $\Delta H_m \approx 35 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta S_m \approx 13 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . The defect-formation enthalpy value derived here is only

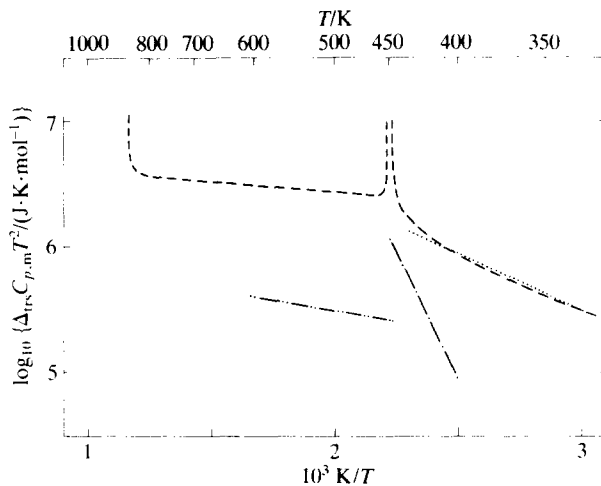


FIGURE 5. Plot for deriving enthalpy of defect formation in  $\beta$ -Ag<sub>2</sub>S. — — —, Present results; ·····, corresponds to  $\Delta H_m = 35 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\text{Ag}^+$  ions, and  $\Delta S_m = 13 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ; ·-·-, results below 450 K by Jost and Kubaschewski;<sup>(3)</sup> - ·- ·-, estimate above 450 K by Schmalzried.<sup>(18)</sup>

a fraction of that claimed by Jost and Kubaschewski:<sup>(3)</sup>  $\Delta H_m = 138 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\alpha\text{-Ag}_2\text{S}$ .

In the phenomenological theory by Gurevich and Kharkats<sup>(17)</sup> the defect formation energy  $W$ , the interaction constant  $\lambda$ , the changed oscillator frequency factor  $\nu$ , and the ratio  $N'/N$  of interstitial to normal lattice sites, are related for a "strong" transition by the equation:

$$\Delta C_{p,m} T^2 = \nu^{1/2} (\lambda^2 X^2 / 2R) \exp(-\lambda X / 2RT), \quad (T < T_{\text{trs}}),$$

and

$$\Delta C_{p,m} T^2 = \nu^{-1} \{ \lambda^2 (X-1)^2 / R \} \exp\{ -\lambda(1-X) / RT \}, \quad (T > T_{\text{trs}}),$$

where  $X = W/\lambda$  and  $\nu = \chi N'/N$ . Application of this expression to  $\text{Ag}_2\text{S}$  leads, as above, to  $W \approx 35 \text{ kJ} \cdot \text{mol}^{-1}$  for  $T < T_{\text{trs}}$ . The pre-exponential factor corresponds to  $\nu \approx 5$ . Combination of the results below and above 450 K results in a large value for the interaction constant  $\lambda$ . This indicates that the transition is not "strong" and calls for a better delineated model.

The thermodynamic approach by Schmalzried<sup>(18)</sup> is devoid of physical modeling, but relates the transitional heat capacity to tangible physical quantities, some of which unfortunately have not yet been determined. The large uncertainty in the presently derived values—mainly through lack of knowledge about the lattice heat capacity—precludes consideration of the behavior of  $\alpha\text{-Ag}_2\text{S}$ . The equation derived by Schmalzried<sup>(18)</sup> for the high-temperature tail of the transition is

$$\Delta C_{p,m} = (R/2)(4T_{\text{max}}/T)^2 \exp(-2T_{\text{max}}/T) \exp\{ -(\Delta S_m^* + R \ln z) / 2R \}.$$

He chose  $\Delta C_{p,m} = 1.25 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at  $T_{\text{max}} \approx T_{\text{trs}} = 450 \text{ K}$  for  $\beta\text{-Ag}_2\text{S}$  as an illustration. These assumptions lead to  $(\Delta S_m^* + R \ln z) = 33 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , where  $\Delta S_m^*$  is the molar entropy of defect formation and  $z$  is the number of equivalent interstitial sites per elementary unit. The resulting curve, see figure 4, shows a transitional heat capacity 6 to 10 times smaller than obtained by us. The present values can be fitted to Schmalzried's equation with  $T_{\text{max}} = 160 \text{ K}$  and  $(\Delta S_m^* + R \ln z) = 51 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . The physical implication of these values is not yet clear.

According to the structural work by Cava *et al.*<sup>(13)</sup> the four silver atoms in the unit cell are in a 12-fold position at 600 K, tetrahedrally coordinated to sulfur, and have restrictions regarding simultaneous occupation of neighboring sites, see below. Complete randomization of the silver atoms would correspond to a structural disorder entropy:

$$\Delta S_m = 6R(0.333 \ln 0.333 + 0.667 \ln 0.667) = 31.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

If the randomization of silver atoms involves excitation to one higher energy level only, the heat-capacity behavior might be approximated by a Boltzmann excitation of the silver atoms from a non-degenerate ground level to a level with degeneracy leading to the same entropy increment as above, *i.e.*

$$\Delta S_m = 2R \ln\{(g_1 + g_0)/g_0\} = 2R \ln 6.74.$$

The high-temperature tail of the corresponding heat-capacity curve, adjusted to the experimental curve at 500 K, is shown in figure 4. The decline is steeper than observed, but this is not unexpected, since the nearest-neighbor tetrahedral sites are too close (171 pm) for simultaneous occupation by silver atoms. In fact, even second-nearest neighbors are barely one  $\text{Ag}^{\text{I}}$ -diameter apart (243 pm against 228 pm for four-coordinated  $\text{Ag}^{\text{I}}$ ).<sup>(49)</sup> The resulting jumping restrictions have been thought to favor a caterpillar-like movement of the silver atoms. Diffuse X-ray-scattering studies by Cava and McWhan<sup>(50)</sup> indicated that the mobile silver atoms are highly correlated in cylindrical domains, one unit cell in diameter and between three and four unit cells long. The correlated motion is thus not confined to a string, but rather to a cylinder, and involves as many as 25 silver atoms at temperatures just above the  $\alpha$ -to- $\beta$  transition for  $\text{Ag}_2\text{S}$ .

A lower limit to the structural disorder entropy is

$$\Delta S_m = 2R \ln 3 = 18.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1},$$

as result of the random distribution of each silver atom on three positions. The related Schottky-type heat-capacity curve is shown in figure 4, again adjusted to the experimental curve at 500 K. The decline in the  $\beta$ - $\text{Ag}_2\text{S}$  region is surprisingly close to that observed, and so is the entropy increase, see figure 6. A lowering of the excitation wavenumber from 685 to 600  $\text{cm}^{-1}$  would give complete correspondence with the observed entropy values for  $\beta$ - $\text{Ag}_2\text{S}$  but is not warranted in view of the approximations made.

The structure of  $\gamma$ - $\text{Ag}_2\text{S}$  is not yet known in detail. It is remarkable, however, that

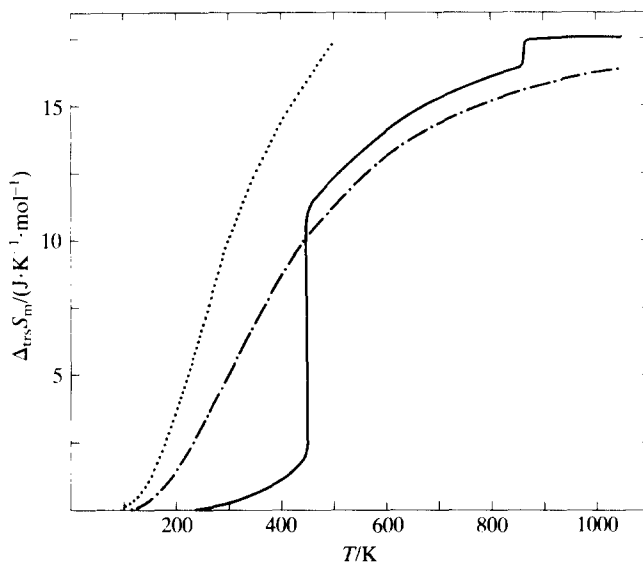


FIGURE 6. Transitional entropy for  $\text{Ag}_2\text{S}$ . —, Present results; - - -, entropy acquired in a Schottky-type transition for  $2\text{Ag}$  with  $g_0/g_1 = 1/2$  and  $\Delta E/hc = 685 \text{ cm}^{-1}$ ; ····, same for  $g_0/g_1 = 1/3$  and  $\Delta E/hc = 593 \text{ cm}^{-1}$ .

the assumption of antiferite structure with lattice constant  $a = 634$  pm at 923 K according to Frueh,<sup>(15)</sup> leads to unreasonably long Ag–S tetrahedral bond distances (275 pm), just as in  $\beta$ -Ag<sub>2</sub>S. Displacement of the silver atoms from the tetrahedral interstice to one of the four surrounding trigonal interstices would result in a more reasonable bond distance (256 pm). Moreover, structural disorder of the silver atoms is presumably retained in  $\gamma$ -Ag<sub>2</sub>S.

Finally, a brief comment is needed on the work by Perrott and Fletcher<sup>(4)</sup> whose peculiar results provided much of the motivation for this study. As already noted, they found a rapidly increasing—albeit reproducible only to  $\pm 10$  per cent—heat capacity, culminating in a transition at 620 K for their stoichiometric sample. Samples with excess silver or sulfur, however, revealed smaller heat capacities, readily reproducible and approximately constant above 450 K. Moreover, the excess disordering enthalpy of the stoichiometric sample was balanced by a correspondingly larger transitional enthalpy around 450 K in the samples with excess of one of the components. Detailed experimental results were not provided by these authors so it is impossible to judge the strength of this assertion. However, this claim was consistent with their earlier report<sup>(51)</sup> of similar behavior in silver(I) iodide, and a theory<sup>(52, 53)</sup> was developed to quantify and model the mechanism for gradual disordering of the stoichiometric compound with temperature, as opposed to complete disordering at one temperature for compositions deviating from exact stoichiometry.

We find no support for a significant difference either in the magnitudes of heat capacity or of the  $\alpha$ -to- $\beta$  transitional enthalpy of Ag<sub>2</sub>S between the stoichiometric sample and that with excess sulfur. We therefore conclude that the Perrott–Fletcher model is inapplicable and consider it important to provide further study on the related substance AgI.

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