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Heat capacity and thermodynamic properties of silver(I) selenide, oP-Ag_2Se from 300 to 406 K and of cI-Ag_2Se from 406 to 900 K: transitional behavior and formation properties

Fredrik Grønvold [a,*], Svein Stølen [a], Yuri Semenov [b]

[a] *Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo, Norway*
[b] *Vernadsky Institute of Geochemistry and Analytical Chemistry, V-334 Moscow, Russia*

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Abstract

Heat capacities of silver sulfide samples in the Ag_2Se composition region have been measured by adiabatic calorimetry from 298.15 to 900 K. In addition to a single-phase sample with stoichiometric composition, a two-phase sample with 1 mol% silver excess, and one with similar selenium excess were studied. The structural transition from orthorhombic Ag_2Se to cubic Ag_2Se started at about 404.0 K in the two former samples on heating, but progressed remarkably slow with temperature for stoichiometric Ag_2Se. The transition was 90% complete at 406.45 K, compared to 96% completion already at 405.59 K for the sample with silver excess. For the selenium-rich sample the transition was 93% complete at 405.8 K, or about 0.6 K below similar completion for the practically stoichiometric Ag_2Se, which thus has the highest transition temperature. A phase diagram complying with the observations is drawn. In contrast to an earlier finding the transitional enthalpy does not vary appreciably with composition; $\Delta_{trs}H = 6824 \pm 20\,J\,mol^{-1}$. Thermodynamic function values for Ag_2Se have been derived and are tabulated for selected temperatures. The composition range of cubic Ag_2Se phase widens with temperature on the Se-rich side and includes the composition $Ag_2Se_{1.01}$ at about 800 K.

Keywords: Thermodynamic properties; Ag_2Se; Adiabatic calorimetry

1. Introduction

The polymorphism of silver(I) selenide, Ag_2Se, at atmospheric pressure was discovered more than 100 years ago by Bellati and Lussana [1] through changes in electrical resistivity and thermal EMF at 406 K. Subsequently they derived heat capacities of the two-phases and the enthalpy of transition by drop calorimetry in a Bunsen-type ice calorimeter up to 460 K [2]. Several thermodynamic studies carried out since that time will be considered in the following. Most surprisingly, Shukla et al. [3] reported that the enthalpy of transition of three samples, one with slight selenium excess, and two with silver excess, differed by about 20% across the very narrow homogeneity range. The results were rationalized in terms of a statistical model involving redistribution of silver atoms over tetrahedral and octahedral sites, taking blocking of close near neighbor sites into consideration. The authors gave no arguments for the assumed drastic change in fractional occupation of the two types of sites for the minutely different compositions. We

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[*] Corresponding author. Tel.: +47-22-85-5599; fax: +57-22-85-5441.
E-mail address: svein.stolen@kjemi.uio.no (F. Grønvold).

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find this behavior rather unlikely and thus in need of reexamination.

The structural characteristics of the polymorphs were gradually revealed. The high-temperature structure was found by Rahlfs [4] to be body-centered cubic. It will be in the following characterized as cI-Ag$_2$Se. In contrast to the two selenium atoms in fixed positions, the four silver atoms were presumed to be distributed over one 6-fold, one 12-fold and one 24-fold position. The distribution has been considered by several authors since that time [3,5–7], but the various preferences remained unconvincing. Finally, in the single-crystal neutron diffraction study by Oliveria et al. [8] only the tetrahedral 12d sites and the octahedral 6b sites of space group Im3m were found to be occupied. The occupancy of 6b was found to be about 30% at 135 and 150 °C, about 20% at 200 °C, and 0 at 300 °C. This decline, and the corresponding increase in the occupancy of the tetrahedral sites from about 18–33% should presumably be accompanied by a configurational heat capacity tail, which might be detected in our high-temperature calorimeter.

The ambient temperature polymorph occurs in nature and has been given the name Naumannite [9]. It has an orthorhombic (primitive) structure which was completely characterized by Wiegers [10], and is designated here as oP-Ag$_2$Se. The structure consists of an essentially body-centered cubic packing of selenium atoms with two types of silver atoms, one in triangular and the other in tetrahedral interstices.

The compositional variability of the phases has been studied in detail by Valverde [11], von Oehsen and Schmalzried [12], Shukla et al. [13], and Rom and Sitte [14] with coulometric titration technique and analysis. Just above the transition temperature the width $\Delta\delta$ of the phase field of cI-Ag$_2$Se is of the order 0.004 relative to Ag$_{2+\delta}$Se, see Fig. 1, which is drawn according to von Oehsen and Schmalzried [12]. Below the transition temperature the width of the homogeneity range decreases to about 1/3 at 392 K, and to about 1/4 at 373 K. According to von Oehsen and Schmalzried [12] the transition temperature is 403 K on the silver-rich side and 405 K on the selenium-rich side. The ordinate in Fig. 1 is locally expanded in this region for clarity.

In the present study one sample with surplus silver, Ag$_{2.01}$Se ($\delta = 0.01$), one with selenium surplus, Ag$_2$Se$_{1.01}$ ($\delta = -0.0198$), and a practically stoichiometric one were examined in our adiabatic high-temperature calorimeter. Energies were in some instances added in small increments in the transition region in order to study the progress of the transition. The total transitional enthalpies were measured repeatedly for all three samples and heat capacities determined up to 900 K for the two-phase samples in order to delineate any major compositional changes of the Ag$_2$Se phase.

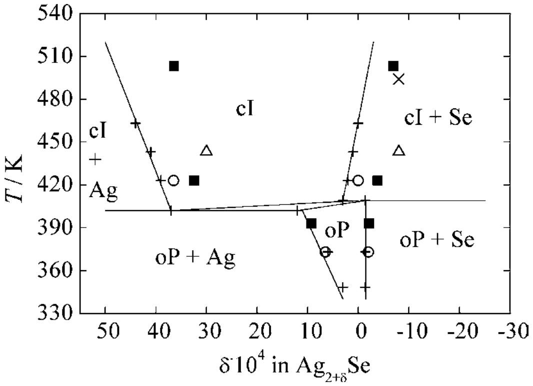

Fig. 1. Phase diagram in the Ag$_2$Se composition region according to the results by von Oehsen and Schmalzried [12], +. cI refers to the phase with body-centered cubic structure, and oP to the one with orthorhombic primitive structure. Results by Valverde [11], ○; von Oehsen and Schmalzried [12], +; Shukla et al. [13], ■; Rom and Sitte [14], △; fusion of selenium in Ag$_2$Se$_{1.01}$, ×.

2. Experimental

2.1. Sample

Crystalline high-purity silver from K.A. Rasmussen, Hamar, Norway was subject to final reduction by dry hydrogen gas for 4 h at 770 K in order to remove traces of water etc. The silver was then degassed in vacuum of 0.5 mPa at 770 K. The selenium was 99.999 mass% pure shot from Koch-Light Laboratories, Colnbrook, England. Mixtures of the elements with compositions Ag$_2$Se and Ag$_{2.01}$Se were heated in evacuated and sealed vitreous silica tubes. The temperature of the mixtures was increased to 770 K during 3 days and maintained at this temperature for 7 days. After crushing, the samples were annealed once more at 770 K for 7 days. The samples were then

Table 1
Unit cell dimensions of Ag_2Se[a]

Authors	*a* (pm)	*b* (pm)	*c* (pm)
Orthorhombic oP-Ag_2Se, Naumannite at ambient temperature			
Zorll [15]	432.5	704.6	782
Conn and Taylor [16]	434.4	711.1	779.0
Austin [17]	432.8	704.4	774.8
Novoselova et al. [18]	433.6	706.7	775.3
Wiegers [10]	433.3	706.2	776.4
Asadov and Yabrailova [19]	432.5	709.0	782.5
Frigstad [20]	433.0 (5)	711.4 (11)	780.8 (10)
Pingitore et al. [21]	433.2	706.5	776.2
Present	433.57 (5)	706.77 (8)	776.43 (7)
Authors	*a* (pm)	*T* (°C)	
Cubic, cI-Ag_2Se			
Rahlfs [4]	499.3 (1.6)[a]	128	
Zorll [15]	497.8	140	
Sharma and Malhotra [22]	498	166	
Asadov and Yabrailova [19]	498	170	
Oliveria et al. [8]	500.6 (1)	135	
Oliveria et al. [8]	501.1 (1)	150	
Oliveria et al. [8]	502.1 (1)	200	
Oliveria et al. [8]	504.3 (1)	300	

[a] Transformed from kX to pm by multiplication by 100,202.

transferred to the calorimetric ampoules, annealed at 670 K for 5 days and cooled to ambient temperature during 1 day. After completion of the measurements the Ag_2Se sample was converted to $Ag_2Se_{1.01}$ by addition of selenium and heat treated at 670 K for 5 days before cooling it to ambient temperature.

Room temperature powder X-ray photographs were taken by the Guinier–Hägg technique using silicon as internal standard and Cu $K\alpha_1$-radiation. Unit cell dimensions for oP-Ag_2Se were derived by least squares refinement. They are listed in Table 1 together with the most precise earlier determinations (four digits). Many additional results are reported in the study by Günther and Keusch [23], and also results for another ambient temperature polymorph with monoclinic or pseudo-tetragonal structure, related to cI-Ag_2Se. It was found to exist in crystal thicknesses up to 20–30 nm. Thicker films transformed into the common stable oP-Ag_2Se. The present results for stoichiometric oP-Ag_2Se agree rather well with those by Wiegers [10] and Pingitore et al. [21].

2.2. Calorimeter

The high-temperature calorimetric apparatus and measuring technique have been described earlier [24,25], along with results obtained for the heat capacity of a standard sample of α-Al_2O_3. The calorimeter is intermittently heated, and surrounded by electrically heated, and electronically controlled adiabatic silver shields. A heated guard system, also of silver, is outside the shields and the whole assembly is placed in a vertical tube furnace. The temperature differences between corresponding parts of the calorimeter and shield are measured by means of $Pt - (Pt + 10\,\text{mass\%}\,Rh)$ thermopiles. The amplified signals are recorded and also used for automatic control of the shield heaters to maintain quasi-adiabatic conditions during input and drift periods. The temperature of the guard body is kept 0.4 K below that of the shield, while the temperature of the furnace is kept 10 K lower to secure satisfactory operation of the control units.

The masses of sample used in the experiments were about 130 g. Each sample was enclosed in an evacuated and sealed vitreous silica tube of about 50 cm^3 volume, which fitted tightly into the silver calorimeter. A central well in the tube served for the heater and the platinum resistance thermometer, which was calibrated locally, at the ice, steam, tin, zinc, and aluminum points. The thermometer resistance was measured with an automatically balancing ASL18 a.c. bridge, operated by a computer. Temperatures are judged to correspond with ITS-90 to within 0.05 K from 300 to 900 K, whereas the resolution of the temperature determination is within 0.00002 K. The energy inputs from a constant-current supply are measured with a Hewlett-Packard digital voltmeter with an accuracy of 0.025%.

The heat capacity of the calorimeter plus empty silica glass container was determined in a separate series of experiments with a standard deviation of a single measurement from the smoothed heat capacity curve of about 0.15%. The heat capacity of the empty calorimeter represented approximately 60% of the total heat capacity. Small corrections were applied for differences in mass of the empty and full vitreous silica containers and for the “zero” drift of the calorimeter.

The computer-operated experiments are started after obtaining a low and steady instrumental temperature drift (<1 mK min^{-1} for a long period). Under ordinary conditions, i.e., when no phase transformation takes place in the sample, the calorimeter temperature reaches its new equilibrium value of about 30–40 min after the end of the input in the ambient temperature range, and within 15 min at 900 K. In transformation regions longer equilibration intervals are used. The standard deviation of a single measurement from the smoothed heat capacity curve is within 0.2%, whereas the accuracy of the determined heat capacity values is judged to be within 0.3%.

3. Results

The heat capacities of Ag_2Se, $Ag_2Se_{1.01}$, and $Ag_{2.01}Se$ are listed in Table 2, and are shown in Fig. 2. A heat capacity maximum signalizing the structural transition at 406 K is present in all three samples. No further transitions were observed in Ag_2Se and $Ag_{2.01}Se$, while for $Ag_2Se_{1.01}$ an additional effect occurred at about 494 K. Another gradual rise in heat capacity started at about 650 K and ceased at about 800 K, see below. The former effect, amounting to 59 J, corresponds to the fusion of 0.00958 Se in the $Ag_2Se_{1.01}$ sample, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (Se) = 6159 J mol^{-1} [26].

The enthalpy of the structural transition at 406 K was determined for all three samples, see Table 3. The values are apparently equal within the uncertainty of the measurements (0.3%), with mean value: $\Delta_{\mathrm{trs}}H_{\mathrm{m}}\,(Ag_2Se) = 6824 \pm 20\ \mathrm{J\,mol^{-1}}$, and $\Delta S_{\mathrm{m}}\,(Ag_2Se) = 16.84 \pm 0.05\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

In the derivation of thermodynamic function values for stoichiometric Ag_2Se the heat capacity results for $Ag_{2.01}Se$ and $Ag_2Se_{1.01}$ were taken into account also, after subtracting the contributions of 0.01 Ag and 0.01 Se, respectively. The results for $Ag_2Se_{1.01}$ above 550 K were disregarded on account of the phase reaction occurring in this region. The heat capacities were fitted by the polynomials $C_p = a + bT + cT^{-2} + dT^3$ from 298 to 406 K, and 406 to 900 K. Values of entropy and enthalpy at 298.15 K were obtained from the heat capacities by Gultyaev and Petrov [27] from 80 to 300 K and those by Walsh et al. [28] from 17 to 283 K. The latter results were adjusted from $Ag_{1.99}Se$ to Ag_2Se through multiplication by the molar mass ratio. Since both series of results were rather close at 80 K, the entropy and enthalpy values by Walsh et al. [28] were adopted without change at this temperature. As our results in the 300 K region were just in the middle between those of the earlier investigators, the latter were combined with equal weight to give $\Delta_0^{298.15}S_{\mathrm{m}}\,(Ag_2Se) = 150.10\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and $\Delta_0^{298.15}H_{\mathrm{m}}\,(Ag_2Se) = 18620\ \mathrm{J\,mol^{-1}}$. These results are used as reference in Table 4.

The formation properties of Ag_2Se (s) in the range 298.15–900 K can now be derived after a proper choice of the enthalpy of formation and functional values for silver and selenium. Those for solid silver are

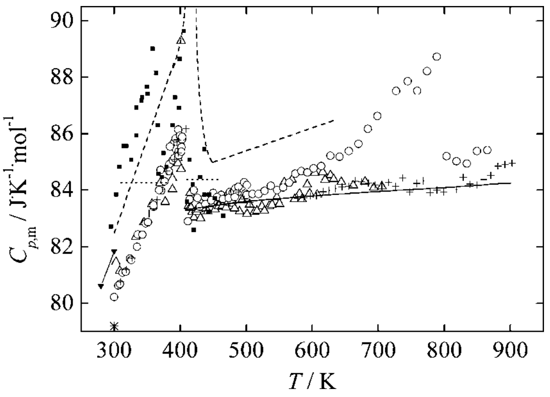

Fig. 2. Heat capacity of Ag_2Se samples. Present results for $Ag_{2.01}Se$ (+), Ag_2Se (△), $Ag_2Se_{1.01}$ (○); Bellati and Lussana [2] (···); Jost and Kubaschewski [34] (−−−); Baer et al. [36] (■); Walsh et al. [28] ▼—▼; Gultyaev and Petrov [27] (✱).

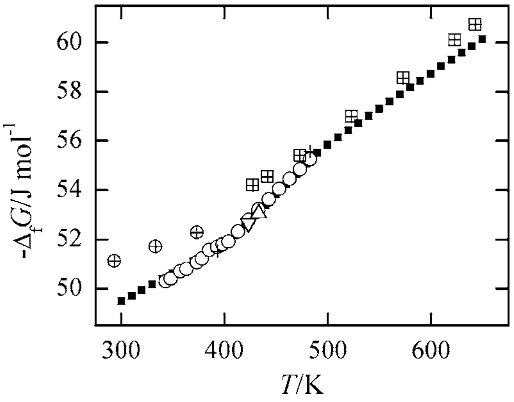

Fig. 3. Gibbs energy of formation of Ag_2Se. Present results taking $\Delta_f H_{\mathrm{m}}$ (298 K) = −42650 J mol^{-1}, ■; Kiukkola and Wagner [32], ⊞; Takahashi and Yamamoto [33], ⊕; Valverde [11], ▽; von Oehsen and Schmalzried [12], ○; Shukla et al. [13], +; Rom and Sitte [14], △.

Table 2
Molar heat capacities of silver (I) selenide

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})
$M(\mathrm{Ag_2Se}) = 294.696\,\mathrm{g\,mol^{-1}}$											
Series I		423.83	83.30	568.99	83.82	430.64	83.03	538.85	83.50	*Series III*	
308.21	81.16	434.03	83.27	580.58	83.88	436.10	83.38	550.20	83.53	377.08	83.60
320.60	81.48	445.09	83.41	592.16	83.56	441.59	83.27	572.97	83.69	388.02	84.43
332.82	82.37	456.19	83.42	603.84	84.15	447.09	83.52	584.42	83.68	396.23	84.97
345.01	82.88	467.36	83.54	615.58	84.14	452.62	83.33	595.95	83.89	401.24	84.76
357.16	83.52	478.57	83.64	627.38	84.03	458.16	83.45	607.51	83.85	Detn. C	
369.33	84.26	489.74	83.87	*Series II*		463.72	83.47	619.31	84.37	416.23	83.39
381.48	84.77	500.95	83.68	387.95	84.04	469.30	83.41	632.07	84.40	427.30	83.33
393.67	85.27	512.16	83.69	396.15	85.14	482.22	83.38	643.88	84.30	*Series IV*	
401.19	89.3	523.42	83.74	Detn. B		493.45	83.65	661.84	84.18	387.88	85.67
Detn. A		534.71	83.76	414.13	83.39	504.73	83.51	679.91	84.31	Detn. D	
412.39	83.46	546.14	84.09	420.64	83.05	516.06	83.29	693.06	84.10	414.96	83.91
418.09	83.25	557.54	84.07	425.18	83.25	527.44	83.29	705.27	84.14		
$M(\mathrm{Ag_2Se_{1.01}}) = 295.486\,\mathrm{g\,mol^{-1}}$											
Series V		471.29	83.66	397.28	85.38	317.33	81.13	446.75	83.65	601.85	84.78
306.03	80.64	473.27	83.85	Detn. F		325.88	81.54	455.58	83.76	613.42	84.86
312.49	81.09	475.27	83.94	*Series VII*		334.36	82.01	464.47	83.69	627.32	85.23
323.89	81.60	477.36	83.58	370.25	84.72	342.77	82.44	473.40	83.73	641.35	85.19
335.63	82.45	479.52	83.92	384.36	85.55	351.13	82.88	482.39	83.76	655.50	85.39
347.67	82.84	481.68	83.96	392.88	85.84	359.44	83.48	491.32	90.57[a]	669.76	85.65
359.70	83.43	483.84	84.07	396.67	86.15	367.73	84.01	500.30	83.84	684.13	86.18
371.19	83.99	486.00	83.90	399.50	85.94	376.04	84.32	509.44	83.87	698.61	86.64
383.64	84.93	488.16	84.13	400.31	85.63	382.50	84.68	518.63	83.87	727.05	87.52
395.56	85.68	490.32	86.14[b]	401.13	85.45	391.14	85.15	527.87	83.98	744.40	87.87
Detn. E		494.54	110.20[b]	401.94	85.53	397.66	85.24	537.16	84.16	758.93	87.53
414.21	83.68	496.60	84.29	402.76	85.80	401.51	85.37	546.51	84.01	773.58	88.23
425.96	83.73	498.76	83.89	403.05	85.90	Detn. H		555.84	84.10	788.32	88.74
437.97	83.75	500.92	84.19	Detn. G		411.71	82.46	564.88	84.27	803.31	85.21
450.03	83.91	*Series VI*		*Series VIII*		420.51	84.00	574.00	84.59	818.32	85.03
462.11	83.84	388.57	85.07	299.90	80.23	429.21	83.43	583.18	84.68	833.88	84.95
469.24	83.73	393.31	85.46	308.68	80.69	437.96	83.51	592.48	84.63	849.35	85.39
										864.93	85.43

Table 2 (*Continued*)

T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{p,\mathrm{m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
$M(\mathrm{Ag_{2.01}Se}) = 295.775\,\mathrm{g\,mol^{-1}}$											
Series IX		391.21	85.10	587.25	83.73	664.84	84.33	747.07	83.94	849.07	84.18
352.51	83.19	396.54	85.32	596.72	83.80	674.83	84.30	757.80	84.24	859.54	84.38
364.61	83.67	Detn. J		606.26	83.80	684.91	84.26	767.93	84.34	870.11	84.53
379.65	84.68	*Series XI*		615.86	83.95	695.06	84.19	778.16	83.92	880.77	84.86
394.77	85.79	309.22	80.77	625.53	83.99	705.30	84.13	788.47	84.01	891.48	84.91
Detn. I		318.14	81.21	635.25	84.06	715.61	84.28	798.83	83.94	902.24	84.96
408.66	86.18	326.97	81.61	645.04	84.12	726.01	84.14	818.03	84.03	488.15	83.94
Series X		577.82	83.72	654.91	84.15	736.49	84.44	828.33	84.46	496.90	83.68
								838.68	84.22	505.73	83.58

[a] $\Delta_{\mathrm{fus}}H$ (Se) $= 59.7\,\mathrm{J}$.

[b] $\Delta_{\mathrm{fus}}H$ (Se) $= 58.4\,\mathrm{J}$.

Table 3
Molar enthalpies of transition for Ag_2Se[a]

T (K)	ΔT (K)	ΔH_m ($J\,mol^{-1}$)	$\Delta H_{m\,(non\text{-}trans)}$ ($J\,mol^{-1}$)	Δt (min)	$\Delta_{trs}H_m$ ($J\,mol^{-1}$)	$\sum \Delta_{trs}H_m$ ($J\,mol^{-1}$)	T_{fin} (K)
$M(Ag_2Se) = 294.696\,g\,mol^{-1}$							
Detn. A							400.4476
401.15	1.41130	126.03	120.70	72	5.4	5.4	401.8589
402.59	1.40043	128.11	119.86	72	8.2	13.6	403.2593
403.86	1.13645	175.55	97.35	72	78.2	91.8	404.3958
404.60	0.34686	347.76	29.70	168	318.1	409.9	404.7246
404.90	0.25158	365.22	21.51	170	343.7	753.6	404.9942
405.13	0.20840	372.45	17.79	168	354.7	1108.3	405.2026
405.32	0.17954	378.69	15.30	171	363.4	1471.7	405.3822
405.50	0.16748	381.23	14.26	172	367.0	1838.7	405.5496
405.66	0.15827	382.95	13.45	172	369.5	2208.2	405.7079
405.87	0.25019	708.84	21.22	351	687.6	2895.8	405.9581
406.02	0.05307	402.06	4.49	172	397.6	3293.4	406.0092
406.12	0.15712	1462.16	13.24	172	1448.9	4742.3	406.1683
406.34	0.28081	1440.00	23.52	171	1416.5	6158.8	406.4491
408.08	3.18881	913.91	265.95	172	648.0	6806.8	409.6379
						6807	
Detn. B							398.9066
402.82	7.82196	7251.74	667.85	124	6583.9	6583.9	406.7286
409.06	4.66472	626.5	388.80	72	237.7	6821.6	411.3933
						6822	
Detn. C							403.4950
405.75	4.51108	7173.52	384.71	112	6788.8	6788.8	408.0061
409.38	2.75083	265.26	229.2	68	36.1	6824.9	410.7570
						6825	
Detn. D							394.1258
399.25	10.25407	1007.26	875.49	50	131.8	131.8	404.3799
406.57	4.38577	7059.77	374.78	68	6685.0	6816.8	408.7656
						6817	
$M(Ag_2Se_{1.01}) = 295.486\,g\,mol^{-1}$							
Detn. E							401.6232
405.05	6.85031	7422.18	583.45	225	6838.7	6838.7	408.4736
						6839	
Detn. F							399.3014
403.27	7.98211	944.20		166	6850.0	6850.0	407.2835
						6850	
Detn. G						404.3256	
404.89	1.12028	132.56	96.29	154	52.2	52.2	405.4459
405.47	0.02257	349.46	1.93	177	347.5	399.7	405.4684
405.45	−0.03050	356.76	−2.62	181	359.4	759.1	405.4379
405.43	−0.01108	353.31	−0.95	182	354.3	1113.4	405.4268
405.42	−0.00442	352.11	−0.38	181	352.5	1465.9	405.4224
405.42	0.00119	351.09	0.10	182	351.0	1816.9	405.4236
405.43	0.00596	350.22	0.51	182	349.7	2166.6	405.4296
405.44	0.02667	1049.01	2.26	366	1046.7	3213.3	405.4562
405.46	0.01465	699.92	1.25	193	698.7	3912.0	405.4709
405.48	0.02272	698.54	1.92	193	696.6	4608.6	405.4936
405.59	0.18686	668.84	15.74	80	653.1	5261.7	405.6805
						5262[b]	

Table 3 (*Continued*)

T (K)	ΔT (K)	ΔH_m ($\mathrm{J\,mol^{-1}}$)	$\Delta H_\mathrm{m\ (non\text{-}trans)}$ ($\mathrm{J\,mol^{-1}}$)	Δt (min)	$\Delta_\mathrm{trs}H_\mathrm{m}$ ($\mathrm{J\,mol^{-1}}$)	$\sum\Delta_\mathrm{trs}H_\mathrm{m}$ ($\mathrm{J\,mol^{-1}}$)	T_fin (K)
Detn. H							403.1654
404.34	2.34880	448.56	201.81	70	246.8	246.8	405.5142
405.52	0.01644	1758.12	1.40	354	1756.7	2003.5	405.5307
405.54	0.02423	876.34	2.06	184	874.3	2877.8	405.5549
405.57	0.02891	875.70	2.45	185	873.2	3751.0	405.5838
405.60	0.03474	874.67	2.94	184	871.7	4622.7	405.6185
405.65	0.05592	871.08	4.71	185	866.4	5489.1	405.6745
405.74	0.14077	862.34	10.99	216	851.4	6340.5	405.8152
406.54	1.44780	610.75	121.88	94	488.9	6829.4	407.2630
						6829	
$M(\mathrm{Ag_{2.01}Se}) = 295.775\,\mathrm{g\,mol^{-1}}$							
Detn. I							401.0100
402.36	2.69611	270.04	231.86	147	38.2	38.2	403.7061
403.47	0.50988	614.89	43.77	129	571.1	609.3	404.2160
404.23	0.02465	701.59	2.11	161	699.5	1308.8	404.2407
404.27	0.05012	696.16	4.28	146	691.9	2000.7	404.2908
404.34	0.09079	689.04	7.73	145	681.3	2682.0	404.3816
404.45	0.12962	682.34	11.00	145	671.3	3353.3	404.5112
404.55	0.07649	691.54	6.48	145	685.1	4038.4	404.5877
404.84	0.50991	1974.76	43.44	296	1931.3	5969.7	405.0976
405.34	0.49251	618.95	41.25	145	577.7	6574.4	405.5901
406.47	1.76095	398.54	148.98	145	249.6	6796.9	407.3515
408.69	2.65329	239.14	221.02	56	18.1	6815.0	410.0043
						6815	
Detn. J							399.2266
403.01	7.56075	7450.14	646.4	122	6812.8	6812.8	406.7873
						6813	

[a] Overall mean value: $6824 \pm 20\,\mathrm{J\,mol^{-1}}$.

[b] Battery failure prevented completion of the measurements.

taken from Cox et al. [29] and the ones for solid and liquid selenium are from Grønvold et al. [30]. Formation results for $\mathrm{Ag_2Se}$ were evaluated by Mills [31], who favored the galvanic cell determinations by Kiukkola and Wagner [32]. These and newer Gibbs energy of formation results are plotted in Fig. 3 together with those obtained here as a best fit with $\Delta_\mathrm{f}H_\mathrm{m}\,(\mathrm{Ag_2Se}, 298.15\,\mathrm{K}) = -42650\,\mathrm{J\,mol^{-1}}$. The resulting values for selected temperatures are found in Table 4 where enthalpies and entropies of formation are also listed.

4. Discussion

The old heat capacity results by Bellati and Lussana [2] failed to demonstrate the rather steep increase in heat capacity of the low-temperature modification as the transition temperature is approached, see Fig. 2. Their results for the high-temperature phase are only about 1% higher than observed here over the common region, 410–460 K: Jost and Kubaschewski's results [34] are about 3% higher up to about 390 K. For the high-temperature phase they are about 2% higher than those obtained here. Honma and Iida [35] presented a graph only, with heat capacities about as by Jost and Kubaschewski [34] at 300 K, but with a less steep rise with temperature. Heat capacity measurements by Baer et al. [36] are even higher than those by Jost and Kubaschewski [34] up to about 363 K where they showed a drop in heat capacity of about $4\,\mathrm{J\,K^{-1}\,mol^{-1}}$, which was ascribed to an unknown transition of the second order. A slightly decreasing heat capacity was observed for the high-temperature

Table 4
Thermodynamic properties of Ag_2Se at selected temperatures, $M(Ag_2Se) = 294.696\,g\,mol^{-1}$

T (K)	$C_{p,m}$	$\Delta_0^T H_m$ ($J\,K^{-1}\,mol^{-1}$)	$\Delta_0^T S_m$ ($J\,K^{-1}\,mol^{-1}$)	$-(\Delta_0^T G_m - \Delta_0^0 H_m)/T$ ($J\,K^{-1}\,mol^{-1}$)	$-\Delta_f H_m$ ($J\,mol^{-1}$)	$\Delta_f S_m$ ($J\,K^{-1}\,mol^{-1}$)	$-\Delta_f G_m$ ($J\,mol^{-1}$)
298.15	80.35	18,620	150.10	87.65	42,650	22.73	49,427
300	80.40	18,769	150.60	88.04	42,642	22.76	49,470
320	81.19	20,384	155.81	92.11	42,546	23.07	49,928
340	82.21	22,018	160.76	96.00	42,440	23.39	50,392
360	83.32	23,673	165.49	99.73	42,322	23.73	50,865
380	84.41	25,351	170.03	103.33	42,191	24.08	51,341
400	85.40	27,049	174.38	106.76	42,048	24.45	51,828
406	85.67	27,562	175.66	107.77	42,004	24.56	51,975
406	83.31	34,386	192.467	107.77	35,180	41.367	51,975
410	83.34	34,720	193.31	108.63	35,163	41.44	52,153
420	83.37	35,553	195.32	110.67	35,123	41.53	52,566
440	83.44	37,221	199.20	114.61	35,050	41.70	53,398
460	83.50	38,891	202.91	118.36	34,984	41.85	54,235
480	83.56	40,561	206.47	121.97	34,927	41.97	55,073
500	83.61	42,233	209.88	125.41	41,084	29.52	55,844
550	83.71	46,416	217.85	133.46	41,389	28.94	57,306
600	83.80	50,604	225.14	140.80	41,691	28.41	58,737
650	83.88	54,796	231.85	147.55	41,998	27.92	60,146
700	83.96	58,992	238.07	153.80	42,316	27.45	61,531
750	84.03	63,192	243.87	159.61	42,653	26.98	62,888
800	84.10	67,395	249.29	165.05	43,020	26.51	64,228
850	84.18	71,602	254.39	170.15	43,427	26.02	65,544
900	84.26	75,813	259.21	174.97	43,885	25.49	66,826

phase in the range of our measurements up to about 470 K.

The heat capacity behavior of the three samples differs remarkably in the 405 K transition region. But both stoichiometric Ag_2Se and $Ag_{2.01}Se$ start to transform measurably at just about 404.0 K, see Table 3 Detn. A and I. The effect presumably signalizes the eutectoid formation of cI-Ag_2Se. For $Ag_2Se_{1.01}$ the effect in starts at 405.5 K, see Table 2, Detn. G and H, and indicates the formation of a more selenium-rich cI-Ag_2Se eutectoid. The close to isothermal transition of the selenium-rich sample, 93% complete at 405.82 K, accords with the very small compositional difference ($\Delta\delta = 0.0003$) between selenium-rich cI-Ag_2Se and oP-Ag_2Se, and thus more rapid equilibration of cI-Ag_2Se when in equilibrium with Se (s).

For our Ag_2Se the progression of the transformation is much more gradual, which might indicate a small silver surplus. It is only about 50% complete at 406.0 K and reaches 90% completion at 406.45 K after 35 h of equilibration. The temperature is now 0.64 K above that for 93% completion in $Ag_2Se_{1.01}$ and calls for a revision of the earlier phase diagram. This is done in Fig. 4 where the homogeneity range of oP-Ag_2Se extends beyond that of oP-Ag_2Se also on the selenium-rich side. It finds support in the re-

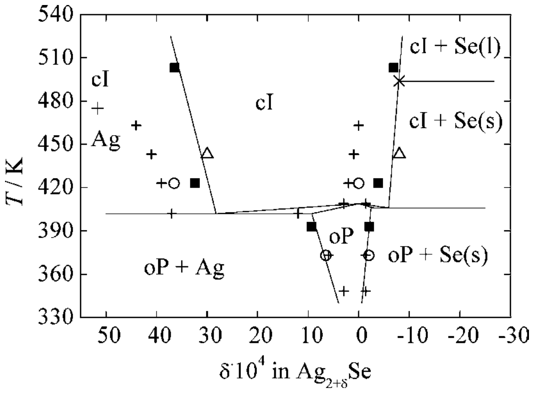

Fig. 4. Revised phase diagram in the Ag_2Se composition region. Experimental observations, see legend in Fig. 1.

sults by Shukla et al. [13], and especially by Rom and Sitte [14] who put the phase limits of cI-$Ag_{2+\delta}Se$ at $\delta = 0.003$ and -0.0008 at 443 K. Our measurements on $Ag_2Se_{1.01}$ showed the presence of a selenium surplus in cI-Ag_2Se at the melting temperature of the selenium, 494 K, corresponding to $\delta = -0.00084$. Thus, in our view the composition region of the low-temperature oP-Ag_2Se phase falls entirely inside that of the high-temperature cI-Ag_2Se phase, with a congruent maximum temperature for the rather closely stoichiometric oP-Ag_2Se transforming into cI-Ag_2Se. This in contrast to the phase diagram by von Oehsen and Schmalzried [12], where a peritectoid disproportioning of oP-Ag_2Se with $\delta = -0.00014$ into cI-Ag_2Se with $\delta = 0.0003$ and a small amount of solid selenium is depicted. Strangely enough, Shukla et al. [3] presented the same type of phase diagram as in Fig. 4, even though δ is more negative at 423 K (-0.000381) than at 393 K (-0.000214) in their Table 1.

For the silver-rich sample $Ag_{2.01}Se$ the progression of the transition with temperature is less sharp than for $Ag_2Se_{1.01}$. This deviation from the expected isothermal behavior presumably relates to slow uptake of silver in the high-temperature phase after precipitation when cooling cI-$Ag_{2.01}Se$ to ambient conditions. A similar, but less pronounced effect occurs in our Ag_2Se sample before the major transformation proceeds at about 405.0 K.

The enthalpy of transition values in the literature vary within wide limits, see Table 5. The drop-calorimetric result by Bellati and Lussana [2] is 1.9% above ours, while the more recent ones range from 6280 J mol^{-1} by DSC [3] for $Ag_{2.00069}Se$ and 7740 J mol^{-1} for $Ag_{1.99990}Se$ up to 10,500 J mol^{-1} through application of the Clapeyron equation [39]. The volume expansion at the transition temperature (1.79 cm^3 mol^{-1}) was presumably an overestimate, as Clark and Rapoports [40] initial pressure dependence of the transition temperature (6.02 K $kbar^{-1}$) would result in $\Delta_{trs}H = 12\,000$ J mol^{-1}.

The spectacular change in molar transitional enthalpy observed by Shukla et al. [3] for minute changes in composition was interpreted with reference to a statistical model involving the distribution of four Ag atoms over 12 tetrahedral and six octahedral positions in the body-centered cubic unit cell. Taking obstruction of neighbor sites into consideration Shukla et al. [3] estimated an increase in the configurational entropy contribution for Ag_2Se in the range 21.3–24.2 J K^{-1} mol^{-1} as the molar tetrahedral occupancy (per Ag or for 1/2 Ag_2Se with three tetrahedral sites) decreased from 0.9 to 0.7. Correspondingly, the fractional site occupation decreases from 0.30 to 0.23. These values are outside the experimental one by Oliveria et al. [8] who found that the tetrahedral occupancy factor was 0.189 ± 0.026 at 409 K. The model by Shukla et al. [3] would thus give

Table 5
Enthalpy of transition of Ag_2Se

Composition	$\Delta_{trs}H_m$ (J mol^{-1})	Method	Authors
Ag_2Se	6,955	Drop	Bellati and Lussana [2]
Ag_2Se	7,020 ± 0,960	Clapeyron	Roy et al. [37]
Ag_2Se	7,030 ± 0,960	Adiabatic	Baer et al. [36]
Ag_2Se	9,875 ± 2,470	DTA	Kulwicki [38]
Ag_2Se	9,160	DTA	Banus [39]
Ag_2Se	10,500	Clapeyron	Banus [39]
Ag_2Se	12,000	Clapeyron	Clark and Rapoport [40]
$Ag_{2.00069}Se$	6,280	DSC	Shukla et al. [3]
$Ag_{2.00038}Se$	7,260	DSC	Shukla et al. [3]
$Ag_{1.99990}Se$	7,740	DSC	Shukla et al. [3]
Ag_2Se	6,740	Adiabatic	Honma and Iida [35]
Ag_2Se	6,730	DSC	Rino et al. [41]
Ag_2Se	6,500	DSC	Pingitore et al. [42]
$Ag_{2.01}Se$	6,824 ± 20	Adiabatic	Present
Ag_2Se	6,824 ± 20	Adiabatic	Present
$Ag_2Se_{1.01}$	6,824 ± 20	Adiabatic	Present

$\Delta_{\mathrm{trs}}S_{\mathrm{m}} = 24.9\,\mathrm{J\,K^{-1}\,mol^{-1}}$, which is even higher than their theoretical structural disorder estimate. The implication by Shukla et al. [3] regarding the large transitional entropy discrepancy and its change with composition was that the low-temperature phase is considerably disordered, and increasingly so as δ in $Ag_{2+\delta}Se$ increases. The reported transitional enthalpy change in the 406 K region corresponds to an entropy increase for $Ag_{2+\delta}Se$ of $3.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for a silver decrease of 0.00079 mol in the cI-Ag_2Se-structure, a highly speculative and presently unfounded supposition.

The molar constant pressure heat capacity of Ag_2Se is rather high, both above and below the 406 K transition. The heat capacity at the lowest temperature measured (17 K) points to a Debye temperature of about 140 K. Thus, the lattice heat capacity at constant volume is expected to reach about 99% of the classical limit ($74.9\,\mathrm{J\,K^{-1}\,mol^{-1}}$) at 350 K already.

As no structural disorder was reported for oP-Ag_2Se, and only negligible electronic and ionic conduction, the anharmonic contribution to the lattice heat capacity appears to be large. It is reflected in the expansivity, which shows the value $\alpha_{\mathrm{V}} = 106.2 \times 10^{-6}\,\mathrm{K^{-1}}$ close to the transition temperature according to Glazov and Makhmudova [43]. Above the transition temperature it is $54.3 \times 10^{-6}\,\mathrm{K^{-1}}$ according to the same authors. The neutron diffraction results by Oliveria et al. [8] give $\alpha_{\mathrm{V}} = 140 \times 10^{-6}\,\mathrm{K^{-1}}$ at 440 K and about $130 \times 10^{-6}\,\mathrm{K^{-1}}$ at 523 K. In the absence of compressibility data the dilation contribution to the heat capacity, $C_{\mathrm{d,m}} = C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \alpha_{\mathrm{V}}\Gamma C_V T$, where $\Gamma = 2$ is tentatively assumed. The resulting $C_{p,\mathrm{m}} \cong 80\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at 350 K falls considerably below the measured value, while $83.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at 440 K and $85.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$ at 523 K are not far away from those measured. The decaying redistribution of the Ag atoms above 440 K according to Oliveria et al. [8] may account for the unusually moderate rise in C_p of 1.0% only from 440 to 900 K.

The observed transitional heat capacity increase of $Ag_2Se_{1.01}$ in the temperature range 550–800 K corresponds to $\Delta_{\mathrm{r}}H = 395\,\mathrm{J\,mol^{-1}}$ for the reaction

$$Ag_2Se\,(s) + 0.01\,Se\,(l) = Ag_2Se_{1.01}\,(s)$$

at 800 K, taking the steadily increasing heat capacity of the product into account. Since the reaction proceeded under close to equilibrium conditions the entropy of $Ag_2Se_{1.01}$ (s) at 800 K should be $S(0.01\,Se) + \Delta_{\mathrm{r}}S = 1.40\,\mathrm{J\,K^{-1}\,mol^{-1}}$ higher than that of Ag_2Se (s). The partial quantities remain unknown, but have been considered at lower temperature and closer to stoichiometry by von Oehsen and Schmalzried [12]. According to these authors the relative (partial) enthalpy of silver decreases from about $12\,\mathrm{kJ\,mol^{-1}}$ for $\delta = 3 \times 10^{-3}$ to about $-25\,\mathrm{kJ\,mol^{-1}}$ for $\delta = 0$ at 443.2 K. Thus, the resulting integral transitional enthalpy does not increase by more than about $5\,\mathrm{J\,mol^{-1}}$. According to Shukla et al. [3] there is an immense transitional enthalpy decrease of the compound as silver is added. That is about 1400 J for the reaction $Ag_2Se\,(s) + 0.00069\,Ag\,(s) = Ag_{2.00069}Se\,(s)$, or at least two orders of magnitude higher than would be expected.

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