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HEAT CAPACITY MEASUREMENTS ON Sn_2S_3 AND THE THERMODYNAMIC FUNCTIONS OF THE TIN SULFIDES

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ABSTRACT

The heat capacity of Sn_2S_3 was measured in the temperature range 110—610 K, employing a computer-interfaced differential scanning calorimeter. The sum of the known heat capacities of SnS and SnS_2 agreed with the measured heat capacity of Sn_2S_3 from 110 to 610 K. Structural and bonding similarities between Sn_2S_3, SnS and SnS_2 justify the extrapolation of the heat capacity of Sn_2S_3 from 110 to 0 K, using the sum of the heat capacities of SnS and SnS_2. With the measured and extrapolated heat capacity data of Sn_2S_3, the absolute entropy, enthalpy and free enthalpy have been evaluated (S^0_{298} = 163.6 ± 6 J K^{-1} $mole^{-1}$, $H^0_{298} - H^0_0$ = 23.7 ± 1 kJ $mole^{-1}$ and $G^0_{298} - H^0_0$ = —25.1 ± 2 kJ $mole^{-1}$) for Sn_2S_3.

INTRODUCTION

Studies of the vaporization of SnS [1a], Sn_2S_3 [1b], and SnS_2 [1b] and characterization of the chemical vapor transport and crystal growth properties of SnS_2 [2] require the knowledge of thermodynamic properties of all compounds involved as a function of temperature. The heat capacities of SnS and SnS_2 have been determined at both low [3] and high [4] temperatures, but the corresponding data for Sn_2S_3 were not available. This paper presents measurements of the heat capacity of Sn_2S_3 in the temperature range 110—610 K. These data are compared to the known heat capacities of SnS and SnS_2 [3,4]. Based on this comparison, the heat capacity of Sn_2S_3 is extrapolated to 0 K using empirical equations. Tabulations of the thermodynamic parameters for all tin sulfides are presented.

EXPERIMENTAL PROCEDURES

Heat capacity instrumentation

A differential scanning calorimeter (Perkin-Elmer DSC-2) was used for the thermal analysis of the Sn_2S_3 samples. An enclosed, air-cooled refrigeration unit (Perkin-Elmer Intracooler II) was attached to the DSC allowing heat capacity measurements to temperatures of 210 K. Using the liquid nitrogen accessory (Perkin-Elmer 319-0027) the lower temperature limit of the heat capacity measurements was extended to 100 K. Continuous transformation of the output amplitudes into digital form was accomplished through the use of an analog/digital converter (Perkin-Elmer Digital Data Recorder). The digital output was recorded on paper punch tape (Iomec Inc.). The range of the digital output is from 0 to 10 000 units, which corresponds to full-scale displacement of the DSC recorder. Heat capacity data points were sampled every 1.2 s.

The heat capacity calculations from the recorded amplitudes were performed on a Hewlett-Packard 9821A programmable calculator. The DSC output on tape was read by an optical tape reader (HP2748B) and assimilated into the calculator. The details of the program used in the evaluation of the heat capacity have been discussed earlier [5].

Benzoic acid (Baker, reagent grade) was used as the calibration standard over the temperature range 100—260 K. Sapphire (Perkin-Elmer 219-036) was used as the standard in the temperature range 210—620 K. The temperature scale was calibrated using various standards as described earlier [6]. The accuracy of the measured temperature is estimated to be ±0.2 K. The accuracy of the heat capacity measurements is estimated to be ±2% in the temperature range 100—300 K [7] and better than ±1% from 300 to 620 K [5].

Sample preparation and pan loading procedures

Tin sesquisulfide, Sn_2S_3, was prepared by annealing stoichiometric amounts of tin (99.999%) and sulfur (99.999%) in previously cleaned [8] and evacuated ampoules of fused silica at about 770 K for 300 h. During the above annealing period, the material was removed from the ampoule and ground repeatedly to ensure complete reaction. The crystallographic identity of the material was established by X-ray diffraction techniques. All reflections of Debye—Scherrer powder photographs (114.59 mm diameter camera, Ni-filtered Cu$K\alpha$ radiation) could be indexed on the basis of an orthorhombic unit cell. The calculated lattice parameters ($a_0 = 0.8771 \pm 0.0017$ nm, $b_0 = 0.3742 \pm 0.0007$ nm, $c_0 = 1.403 \pm 0.003$ nm) were in good agreement with literature values [9—11]. Prior to loading the samples into the aluminum pans, the material was outgassed at about 375 K for 2 h at a pressure of about 10^{-4} Pa.

For the heat capacity measurements, all samples were loaded and sealed in aluminum pans in a dry box containing a desiccated nitrogen atmosphere. Hermetically sealed pans were used in the heat capacity measurements from 220 to 610 K. Non-hermetically sealed pans were used in the low temperature measurements (110—260 K) to accommodate larger amounts of samples. The low temperature heat capacity measurements did not require hermetic sealing of the pans since reactions of the sample under these temperature conditions are unlikely. The mass of the powdered sample was determined by weighing the pan and cover before and after loading using a Cahn microbalance with an accuracy of ±0.02 mg. The pans were filled with sample and sealed to minimize the free volume containing nitrogen. At the end of each heat capacity run, the sample plus pan were weighed to confirm constant mass. In all cases the mass of the sample plus pan remained constant within ±0.02 mg for total weights of about 60 mg. Microscopic examination of the opened pans revealed no visible reaction between the samples and the aluminum containers.

Heat capacity measurements

In the first run, the heat capacity of Sn_2S_3 was measured in the temperature range 100—260 K using a sample mass of 53.62 mg. The heat capacity data were obtained in temperature intervals of 40 K using a heating rate of 20 K min^{-1} with a sensitivity of 21 mJ s^{-1}. The sample was then cooled to 100 K and the heat capacity measurement was repeated.

In the second and third runs, Sn_2S_3 samples of masses 40.11 and 39.22 mg, respectively, were used. Heat capacity measurements for each of these samples were recorded from 220 to 610 K at a heating rate of 10 K min^{-1} and a sensitivity of 21 mJ s^{-1} in temperature intervals of 40—70 K. After completion of a run for a given sample, the sample was cooled to 210 K and the heat capacity measurement was repeated.

RESULTS

The results of the heat capacity measurements on Sn_2S_3 in the temperature range 110—610 K are represented graphically in Fig. 1. (Because of the overlap of experimental data obtained from the individual runs, only part of the 184 individual heat capacity data appears in Fig. 1.) The determination of the heat capacity of Sn_2S_3 was terminated at or near 610 K. Above 610 K thermal effects attributable to the thermal decomposition of Sn_2S_3 were observed [1b].

A least-squares treatment of all the heat capacity data yields the equation

$$\ln C_p^\circ = 0.0991872(\ln T)^3 - 1.85497(\ln T)^2 + 11.6663 \ln T - 19.8237 (\mathrm{J\ K^{-1}\ mole^{-1}}) \qquad (1)$$

which is valid over the temperature range 110—610 K. The standard devia-

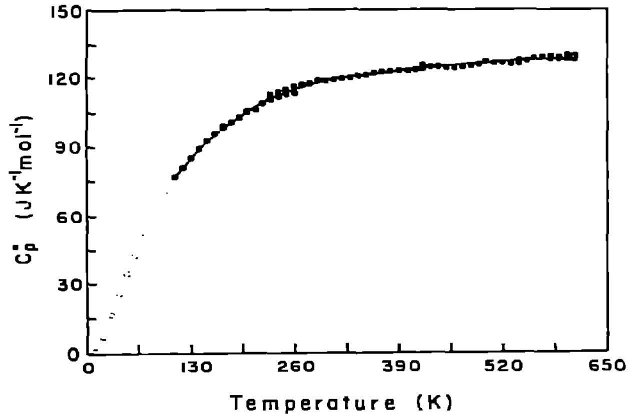

Fig. 1. The heat capacity of Sn_2S_3 as a function of temperature. (●) selected measured heat capacity data; (○) extrapolation of the heat capacity to absolute zero.

tion of experimental heat capacity data from eqn. (1) is ±0.78 J K^{-1} $mole^{-1}$ with a root-mean-square deviation of ±0.7% for all data.

DISCUSSION

The calculation of the thermodynamic parameters $H^0_T - H^0_0$, S^0_T and $G^0_T - H^0_0$ from measured heat capacity data requires a knowledge of the heat capacity to temperatures close to absolute zero. Unfortunately, instrument limitations prevented measurements below 100 K. Because of the anisotropic structure of Sn_2S_3 as discussed below, a representation of the measured heat capacity data based on the Debye equation [12]

$$\frac{C_v}{15\,R} = D\left(\frac{\theta_D}{T}\right) \tag{2}$$

for the temperatures of this study is not expected to be satisfactory.

The low and high temperature heat capacities of SnS and SnS_2 have been investigated earlier [3,4]. A structural comparison of the tin sulfides SnS, Sn_2S_3 and SnS_2 suggested bonding similarities in these compounds [11]. This would allow an extension of Kopp's rule [13] to yield the low temperature (0—100 K) heat capacity of Sn_2S_3 as the sum of the heat capacities of SnS and SnS_2 [3,4].

Sn_2S_3 crystallizes in an orthorhombic structure [9—11] with di- and tetravalent Sn atoms [10,11]. The average length of the Sn(IV)—S bonds in Sn_2S_3 is about 0.256 nm and nearly equals that of the Sn(IV)—S bonds (0.258 nm) in SnS_2 [14]. The average Sn(II)—S bond length in Sn_2S_3 is 0.268 nm, which closely approximates the average of the shorter Sn(II)—S bonds (0.266 nm) in SnS [15]. The structure of SnS is orthorhombic [15] with the same space group as that of Sn_2S_3 [10,11]. Similarities between the hexagonal [14] structure of SnS_2 and the structure of Sn_2S_3 have been reviewed earlier [11]. These similarities show that the tin—sulfur bonds in Sn_2S_3 closely resemble the corresponding bonds in SnS and SnS_2.

In order to demonstrate that the measured heat capacity of Sn_2S_3 in the range 110—610 K approximates the sum of the heat capacities of SnS and SnS_2, a re-evaluation of the earlier data [3,4] for the temperature range of the present study was required.

The heat capacity of SnS

The low temperature heat capacity of SnS has been measured in the temperature range 52.45—298.15 K [3], and the results were empirically fitted [3] to the equation

$$\frac{C^0_p}{3\,R} = D\left(\frac{146}{T}\right) + E\left(\frac{311}{T}\right) \qquad (51\text{—}150\ \text{K}) \tag{3}$$

The quantity $D(146/T)$ represents the Debye function [12] with a θ-temperature of 146 K. The term $E(311/T)$ is the Einstein function [16] with a θ-temperature of 311 K.

TABLE 1

Calculated thermodynamic parameters for SnS(s) [a]

T (K)	C_p^0 (J K^{-1} mole^{-1})	$H_T^0 - H_0^0$ (J mole^{-1})	S_T^0 (J K^{-1} mole^{-1})	$-(G_T^0 - H_0^0)$ (J mole^{-1})
0.0	0	0	0	0
10.0	0.62	3.12	0.31	
20.0	4.32	27.82	1.70	6.24
30.0	9.68	97.79	4.39	34.05
40.0	14.52	218.8	7.82	94.14
50.0	18.79	385.3	11.52	190.5
60.0	22.60	592.3	15.28	324.5
70.0	26.13	835.9	19.03	496.1
80.0	29.14	1112	22.72	705.1
90.0	31.82	1417	26.31	950.5
100.0	34.12	1747	29.78	1231
110.0	36.47	2102	33.16	1546
120.0	38.14	2475	36.41	1894
130.0	39.57	2864	39.52	2274
140.0	40.80	3266	42.50	2684
150.0	41.85	3679	45.35	3123
160.0	42.76	4102	48.08	3591
170.0	43.56	4534	50.70	4085
180.0	44.25	4973	53.21	4604
190.0	44.87	5419	55.62	5148
200.0	45.41	5870	57.93	5716
210.0	45.90	6327	60.16	6307
220.0	46.34	6788	62.31	6919
230.0	46.74	7254	64.38	7553
240.0	47.10	7723	66.37	8206
250.0	47.44	8196	68.30	8880
260.0	47.75	8672	70.17	9572
270.0	48.04	9150	71.98	10283
273.15	48.12	9302	72.53	10510
280.0	48.31	9632	73.73	11011
290.0	48.57	10116	75.45	11757
298.15	48.77	10513	76.78	12377
300.0	48.81	10603	77.08	12519
320.0	49.28	11584	80.24	14093
340.0	49.72	12574	83.24	15728
360.0	50.14	13573	86.10	17422
380.0	50.56	14580	88.82	19171
400.0	50.97	15595	91.42	20974
450.0	52.01	18169	97.49	25699
500.0	53.10	20797	103.0	30714
550.0	54.26	23480	108.1	35995
600.0	55.50	26224	112.9	41522
650.0	56.82	29032	117.4	47281
700.0	58.24	31908	121.7	53259
750.0	59.74	34857	125.7	59444
800.0	61.34	37883	129.6	65829
850.0	63.02	40992	133.4	72406
870.0	63.72	42260	134.9	75089
875.0 (β)	63.90	42578	135.3	75764
875.0 (α)	54.55	43247	136.0	75764
900.0	54.94	44615	137.6	79181
950.0	55.72	47382	140.5	86134
1000.0	55.50	50187	143.4	93234
1050.0	57.28	53032	146.2	100474
1100.0	58.06	55915	148.9	107851
1150.0	58.84	58838	151.5	115361
1153.0	58.89	59014	151.6	115815

[a] The number of figures reported in columns 2, 3, 4 and 5 has only calculational significance.

The high-temperature heat capacity of SnS was later determined from 298.15 to 1225 K [4]. A phase transformation of SnS at 875 K reported earlier [4] was recently identified as a transition from a distorted NaCl to the orthorhombic TlI-type structure [17,18].

To facilitate a direct comparison of the heat capacity of SnS with that of Sn_2S_3, the heat capacity of SnS was computed or interpolated at rounded temperatures in increments of 10—50 K. The results are shown in Table 1. In addition, the thermodynamic parameters $H^0_T - H^0_0$, S^0_T and $-(G^0_T - H^0_0)$ were calculated from the heat capacity of SnS in Table 1 and are listed in columns 3, 4 and 5, respectively.

The heat capacity function of SnS

$$\ln C^0_p = 0.114905(\ln T)^3 - 1.99273(\ln T)^2 + 11.6659 \ln T - 19.1440 (\mathrm{J\ K^{-1}\ mole^{-1}}) \tag{4}$$

was obtained from a least-squares analysis of the data of SnS in the temperature range 100—875 K. The standard deviation of the experimental heat capacity data [3,4] from eqn. (4) is ±0.24 J K^{-1} $mole^{-1}$ with a root-mean-square deviation of ±0.5%.

The heat capacity of SnS_2

The low-temperature heat capacity of SnS_2 was measured from 52.75 to 298.15 K [3]. The data were empirically fitted [3] to the equation

$$\frac{C^0_p}{3R} = D\left(\frac{172}{T}\right) + E\left(\frac{369}{T}\right) + E\left(\frac{415}{T}\right) \qquad (51\text{—}170\ \mathrm{K}) \tag{5}$$

The quantities $D(172/T)$ with a θ-temperature of 172 K, $E(369/T)$ and $E(415/T)$ with θ-temperatures of 369 and 415 K, respectively, represent the Debye [12] and Einstein functions [16].

The high-temperature heat capacity of SnS_2 was later measured from 298.15 to 1005 K [4]. To facilitate a direct comparison of the earlier heat capacity measurements on SnS_2 [3,4] with that of Sn_2S_3, the heat capacity of SnS_2 was computed or interpolated at rounded temperatures in increments of 10—50 K.

The results are shown in Table 2. The thermodynamic quantities $H^0_T - H^0_0$, S^0_T and $-(G^0_T - H^0_0)$ were computed from the heat capacity data of SnS_2 in Table 2 and are listed in columns 3, 4 and 5, respectively.

A least-squares treatment of the heat capacity data of SnS_2 of earlier authors [3,4] in the temperature range 100—1005 K yielded the relationship

$$\ln C^0_p = 0.112224(\ln T)^3 - 2.10132(\ln T)^2 + 13.2230 \ln T - 23.6488 (\mathrm{J\ K^{-1}\ mole^{-1}}) \tag{6}$$

The standard deviation of the heat capacity data [3,4] from eqn. (6) is ±0.38 J K^{-1} $mole^{-1}$ with a root-mean-square deviation of ±0.7%.

TABLE 2

Calculated thermodynamic parameters for $SnS_2(s)$ [a]

T (K)	C_p^0 ($J\ K^{-1}\ mole^{-1}$)	$H_T^0 - H_0^0$ ($J\ mole^{-1}$)	S_T^0 ($J\ K^{-1}\ mole^{-1}$)	$-(G_T^0 - H_0^0)$ ($J\ mole^{-1}$)
0.0	0	0	0	0
10.0	0.38	1.91	0.19	
20.0	2.86	18.11	1.10	3.82
30.0	7.26	68.68	3.02	21.93
40.0	11.76	163.8	5.70	64.23
50.0	16.00	302.6	8.77	135.9
60.0	20.11	483.1	12.05	239.6
70.0	24.68	707.1	15.48	376.8
80.0	29.08	975.9	19.06	549.3
90.0	33.49	1289	22.74	758.1
100.0	37.55	1644	26.48	1004
110.0	41.80	2044	30.29	1288
120.0	45.06	2479	34.07	1610
130.0	47.97	2944	37.80	1969
140.0	50.56	3437	41.45	2366
150.0	52.87	3954	45.02	2798
160.0	54.93	4494	48.50	3266
170.0	56.76	5052	51.88	3768
180.0	58.40	5628	55.17	4303
190.0	59.87	6220	58.37	4871
200.0	61.19	6825	61.48	5470
210.0	62.37	7443	64.49	6070
220.0	63.43	8072	67.42	6760
230.0	64.39	8711	70.26	7448
240.0	65.25	9360	73.02	8164
250.0	66.04	10016	75.70	8908
260.0	66.75	10679	78.30	9678
270.0	67.39	11350	80.83	10473
273.15	67.58	11563	81.61	10729
280.0	67.98	12027	83.29	11294
290.0	68.52	12710	85.69	12139
298.15	68.92	13270	87.59	12845
300.0	69.01	13397	88.02	13008
320.0	69.88	14787	92.50	14813
340.0	70.62	16192	96.76	16706
360.0	71.26	17611	100.8	18682
380.0	71.82	19042	104.7	20738
400.0	72.31	20483	108.4	22869
450.0	73.34	24125	116.7	28506
500.0	74.20	27815	124.7	34551
550.0	74.97	31544	131.8	40968
600.0	75.70	35311	138.4	47726
650.0	76.44	39114	144.5	54800
700.0	77.20	42955	150.2	62168
750.0	77.99	46834	155.5	69812
800.0	78.82	50754	160.0	77716
850.0	79.70	54717	165.4	85867
900.0	80.63	58725	170.0	94252
950.0	81.62	62781	174.4	102861
1000.0	82.65	66888	178.6	111685

[a] The number of figures reported in columns 2, 3, 4 and 5 has only calculational significance.

Thermodynamic properties of Sn_2S_3

Table 3 shows the thermodynamic data for Sn_2S_3. A comparison of the heat capacity of Sn_2S_3 computed in the temperature range 100—650 K from eqn. (1) with the sum of the heat capacities of SnS (Table 1) and SnS_2 (Table 2) shows close correspondence. The relationship

$$C_p^0(Sn_2S_3) = C_p^0(SnS) + C_p^0(SnS_2) \tag{7}$$

is accurate within ±2%. Based on the bonding and structural similarities of these compounds discussed above, this result is expected.

Because of the close agreement of the heat capacity of Sn_2S_3 based on eqn. (1) with the results of eqn. (7) in the temperature range 100—650 K, we propose that the low-temperature heat capacity of Sn_2S_3 can similarly be estimated at lower temperatures by the sum of the heat capacities of SnS and SnS_2. The results of the calculations are entered in Table 3 for the temperature range 0—100 K.

From the heat capacity data of Sn_2S_3 (Table 3), the thermodynamic quantities $H_T^0 - H_0^0$, S_T^0 and $-(G_T^0 - H_0^0)$ were calculated at various temperatures and are listed in columns 3, 4 and 5, respectively.

The absolute entropy, enthalpy and free enthalpy of Sn_2S_3 were thus determined to be $S_{298}^0 = 163.6 \pm 6$ J K^{-1} $mole^{-1}$, $H_{298}^0 - H_0^0 = 23.7 \pm 1$ kJ $mole^{-1}$ and $G_{298}^0 - H_0^0 = -25.1 \pm 2$ kJ $mole^{-1}$, respectively. The absolute entropy of Sn_2S_3 based on heat capacity measurements compares favorably with the entropy value (170.5 ± 6 J K^{-1} $mole^{-1}$) determined from Knudsen effusion studies [1b].

Kelley has tabulated entropy constants for elements which, when added appropriately yield the absolute entropy of compounds [19]. Using these entropy data [19], the absolute entropy of Sn_2S_3 is calculated to be $S_{298}^0 = 160.2 \pm 8$ J K^{-1} $mole^{-1}$.

SUMMARY AND CONCLUSIONS

The heat capacity of Sn_2S_3 was determined in the temperature range 110—610 K. Extrapolation of the heat capacity of Sn_2S_3 from 110 to 0 K was done by summing the empirical heat capacity equations of SnS and SnS_2 [3]. The addition of the heat capacities of SnS and SnS_2 to yield that of Sn_2S_3 is based on structural and bonding similarities between these compounds.

The thermodynamic quantities $H_T^0 - H_0^0$, S_T^0 and $-(G_T^0 - H_0^0)$ were calculated from 0 to 650 K. The absolute entropy of Sn_2S_3 at 298 K is 163.6 ± 6 J K^{-1} $mole^{-1}$. This value agrees favorably with the absolute entropy obtained from Knudsen effusion studies ($S_{298}^0 = 170.5$ J K^{-1} $mole^{-1}$) [1b] and from Kelley's entropy constants [19] ($S_{298}^0 = 160.2$ J K^{-1} $mole^{-1}$). Recent studies on the heat capacities of I—III—VI_2 compounds revealed similar additive relationships for these materials [20].

TABLE 3

Calculated thermodynamic parameters for Sn_2S_3(s) [a]

T (K)	C_p^0 (J K^{-1} mole^{-1})	$H_T^0 - H_0^0$ (J mole^{-1})	S_T^0 (J K^{-1} mole^{-1})	$-(G_T^0 - H_0^0)$ (J mole^{-1})
0.0	0	0	0	0
10.0	1.01	5.03	0.50	
20.0	7.17	45.92	2.80	10.06
30.0	16.94	166.5	7.42	55.98
40.0	26.28	382.6	13.52	158.4
50.0	34.79	687.9	20.29	326.5
60.0	42.97	1077	27.35	564.1
70.0	50.91	1546	34.57	873.4
80.0	58.46	2093	41.86	1255
90.0	65.45	2713	49.15	1711
100.0	71.78	3399	56.37	2238
110.0	75.94	4129	63.33	2837
120.0	81.15	4915	70.16	3505
130.0	85.77	5750	76.85	4240
140.0	89.86	6629	83.36	5041
150.0	93.49	7546	89.68	5906
160.0	96.71	8497	95.82	6834
170.0	99.57	9479	101.8	7822
180.0	102.1	10487	107.5	8869
190.0	104.4	11520	113.1	9972
200.0	106.4	12574	118.5	11130
210.0	108.3	13648	123.8	12342
220.0	109.9	14739	128.8	13605
230.0	111.4	15846	133.8	14918
240.0	112.8	16967	138.5	16279
250.0	114.0	18101	143.2	17688
260.0	115.1	19246	147.7	19142
270.0	116.1	20402	152.0	20641
273.15	116.4	20768	153.4	21122
280.0	117.0	21567	156.3	22182
290.0	117.8	22742	160.4	23765
298.15	118.5	23704	163.6	25086
300.0	118.6	23924	164.4	25389
320.0	120.0	26310	172.1	28754
340.0	121.1	28721	179.4	32270
360.0	122.1	31153	186.3	35927
380.0	123.0	33605	193.0	39721
400.0	123.8	36073	199.3	43644
450.0	125.4	42305	214.0	53982
500.0	126.8	48613	227.3	65018
550.0	128.1	54987	239.4	76690
600.0	129.3	61421	250.6	88944
650.0	130.5	67915	261.0	101737

[a] The number of figures reported in columns 2, 3, 4 and 5 has only calculational significance.

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REFERENCES

1 (a) H. Wiedemeier and F.J. Csillag, Thermochim. Acta, 34 (1979) 257.
(b) H. Wiedemeier and F.J. Csillag, to be published.
2 H. Wiedemeier and F.J. Csillag, J. Cryst. Growth, 46 (1979) 189.
3 E.G. King and S.S. Todd, J. Am. Chem. Soc., 75 (1953) 3023.
4 R.L. Orr and A.U. Christensen, J. Phys. Chem., 62 (1958) 124.
5 U. Gaur, A. Mehta and B. Wunderlich, J. Therm. Anal., 13 (1978) 71.
6 B. Wunderlich and R.C. Bopp, J. Therm. Anal., 6 (1974) 335.
7 U. Gaur and B. Wunderlich, to be published.
8 H. Wiedemeier and A.G. Sigai, J. Cryst. Growth, 6 (1969) 67.
9 S. Mosburg, D.R. Ross, P.M. Bethke and P. Toulmin, Geol. Hydrol. Sci., 273 (1961) 347.
10 D. Mootz and R. Kunzman, Acta Crystallogr., 15 (1962) 913.
11 D. Mootz and H. Puhl, Acta Crystallogr., 23 (1967) 471.
12 P. Debye, Ann. Phys., 39 (1912) 789.
13 H. Kopp, Ann. Chem. Pharm. Suppl., 3 (1864) 289.
14 I. Oftedal, Z. Phys. Chem., 134 (1928) 301.
15 W. Hofmann, Z. Kristallogr., 92 (1935) 161.
16 A. Einstein, Ann. Phys., 39 (1912) 789.
17 H. Wiedemeier and F.J. Csillag, Z. Kristallogr., 149 (1979) 17.
18 H. Wiedemeier and H.G. von Schnering, Z. Kristallogr., 148 (1978) 295.
19 J.L. Margrave, The Characterization of High Temperature Vapors, Wiley, New York, 1967.
20 K.J. Bachmann, F.S.L. Hsu, F.A. Thiel and H.M. Kasper, J. Electron. Mater., 6 (1977) 431.