Low-temperature heat capacities of molybdenum diselenide and ditelluride [a]

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The low-temperature heat capacities of $MoSe_2$ and $MoTe_2$ have been determined for technological and scientific reasons. Both compounds in their hexagonal form have a lamellar sandwich-layer structure and in confirmation of extant data on molybdenite, MoS_2, these compounds are shown to follow the Debye limiting law for heat capacity at low temperature despite contrary indications in the literature. At 298.15 K the heat capacity C_p, entropy $S°$, and Gibbs energy in the form $\{G°(T) - H°(0)\}/T$ are (for $MoSe_2$) 16.87, 21.29, and -10.33 cal_{th} K^{-1} mol^{-1}; and (for $MoTe_2$) 18.38, 27.55, and -14.60 cal_{th} K^{-1} mol^{-1}.

1. Introduction

Molybdenum is among the fission products produced in highest yield in nuclear reactors and the thermodynamics of its chalcogenide compounds is, therefore, important in the technology of fuel elements and coolant systems in nuclear reactors. Moreover, the chalcogenide compounds are used as high-temperature lubricants. Since a contrary finding existed in the literature as to the temperature dependence of the heat capacity of molybdenite prior to our recently published study,[1] additional confirmation was a desideratum. Although the ultimate conformity of MoS_2 with the Debye limiting-law heat-capacity behavior has been demonstrated, it was considered worthwhile to show that this was no accident of relative atomic masses or other artifacts but obtained as well for the similarly structured selenide and telluride compounds. All three hexagonal lattices possess a lamellar sandwich-layer type structure and taken together involve a four-fold range of relative atomic masses.

2. Experimental

APPARATUS

Heat capacity measurements were made in the Mark II adiabatic cryostat which has been described previously.[2] The samples were contained in a gold-plated copper

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calorimeter (laboratory designation W-48), incorporated a gold-gasketed seal, gold-plated copper vanes to enhance conductivity, a mass of 33.4657 g, and an internal volume of 44.44 cm^3. To facilitate rapid thermal equilibration, small amounts of helium gas (about 70 Torr) were introduced.† The temperature of the calorimeter was measured with a platinum capsule-type 25 Ω (nominal) resistance thermometer (laboratory designation A-5) inserted into a re-entrant well in the calorimeter after calibration by the National Bureau of Standards. The resultant temperature scale was judged to correspond to the IPTS-68 to within 0.03 K from 10 to 90 K and within 0.04 K from 90 to 350 K. A 150 Ω constantan heater wound (non-inductively) on a cylindrical gold-plated copper heater core surrounds the resistance thermometer.

The chalcogenides (MoSe$_2$, MoTe$_2$) were loaded directly into the calorimeter, since they are stable in air at room temperatures. The calorimeter within a stainless-steel vessel connected to a high-vacuum line was evacuated, a small amount of helium gas was introduced to aid thermal equilibration, and then the calorimeter was sealed by forcing the gold gasket with a screw closure, against the knife-edged aperture (approximately 1 cm in diameter) on the calorimeter. The calorimeter seal was then tested for tightness *in situ*. It was then brought to constant mass (subject to room temperature, atmospheric pressure, and relative humidity adjustments) and Apiezon-T grease was added in quantity equal to that present during the separate heat-capacity determinations of the calorimeter + heater + thermometer assembly.

The masses, molar masses, densities, and helium gas pressures used for both chalcogenides are summarized in table 1. Heat-capacity measurements were made

TABLE 1. MoS$_2$ and MoTe$_2$ sample details: molar mass M, sample mass m, density ρ, and helium pressure p(He)
(Torr = 101 325/760) Pa

Compound	M/g mol^{-1}	m/g	ρ/g cm^{-3}	p(He)/Torr
MoSe$_2$	253.86	100.2236	6.96 [a]	65
MoTe$_2$	351.14	100.4699	7.78 [b]	78

[a] Compare reference 3.
[b] Compare reference 4.

by the intermittent adiabatic technique. Accuracy is assured by ultimately referring all determinations of mass, temperature, resistance, and potentials to calibrations performed by the National Bureau of Standards and by the measurement of heat capacity of standards established by the Calorimetry Conference.[5]

SAMPLE PROVENANCE

The samples of molybdenum diselenide and ditelluride were purchased from Alpha Inorganics and were claimed to be more than 99 moles per cent pure. Both were fine powders, had a black-gray metallic color, and were slippery to the touch. X-ray

† Throughout this paper Torr = (101 325/760) Pa; cal$_{th}$ = 4.184 J.

powder diffraction patterns for $MoTe_2$ and $MoSe_2$ were taken to characterize both as α-phase (hexagonal). No impurities were detected; only two very weak extra lines were found and the deduced cell parameters agreed well with literature values.[6, 7]

3. Results

The heat capacities were corrected for curvature.[8] The results are expressed in terms of molar masses on the 1968 scale of atomic weights. The smoothed heat capacities and the thermodynamic functions, at selected temperatures, were obtained by fitting a polynomial through the experimental points by least squares and integrating the resulting functions. Below 5 K the heat capacities were extrapolated from a plot of C_p/T against T^2 as depicted in figure 1.
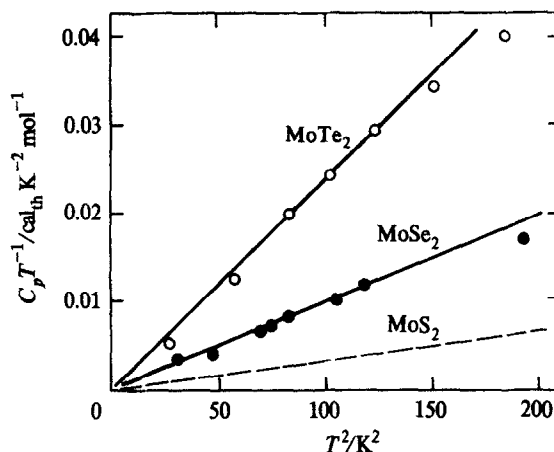

FIGURE 1. Plot of C_p/T against T^2 for MoS_2, $MoSe_2$, and $MoTe_2$.

The heat capacities at constant pressure, C_p, are presented in table 2 and depicted graphically in figure 2. The thermodynamic functions obtained by digital computer quadrature are reported in tables 3 and 4 at selected temperatures.

It is to be noted that although the columns in tables 3 and 4 are headed as absolute quantities, the extrapolations between 0 and 5 K assume the absence of any anomalies in the heat capacity.

4. Discussion

The plots of $\log C_p$ against $\log T$ for MoS_2, $MoSe_2$, and $MoTe_2$ in figure 3 all indicate that there is no region in which the low-temperature heat capacity is represented explicitly by a T^2 limiting law over a finite temperature range. Rather, for all three at the lowest temperatures an obvious trend to the usual Debye T^3-limiting law occurs. A short temperature range in each over which the tangent to the heat capacity curve

TABLE 2. Heat capacities of molybdenum diselenide and ditelluride

$(\text{cal}_{th} = 4.184 \text{ J})$

$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$	$\dfrac{T}{K}$	$\dfrac{C_p}{\text{cal}_{th}\,K^{-1}\,mol^{-1}}$
				Molybdenum diselenide (MoSe₂)			
Series I		211.26	15.37	Series IV		Series V	
62.29	5.221	221.37	15.62	10.92	0.130	8.661	0.064
68.20	5.985	231.35	15.83	13.93	0.237	9.183	0.077
74.00	6.709	241.22	16.02	15.13	0.288		
80.43	7.495	251.00	16.17	16.33	0.342		
87.40	8.323	261.42	16.36	17.61	0.399		
95.45	9.151	271.74	16.15	18.95	0.466	Series VI	
105.49	10.09			20.44	0.550	5.55	0.078
116.26	11.00			22.20	0.657	7.09	0.034 [a]
126.31	11.75			24.07	0.783	8.26	0.055 [a]
136.10	12.40	Series III		25.79	0.913	9.30	0.083
		258.10	16.33	27.50	1.053	10.30	0.110
Series II		268.94	16.49	29.73	1.248	11.39	0.140
138.82	12.58	279.68	16.63	32.32	1.498	12.54	0.180
149.53	13.18	290.33	16.76	35.45	1.827	37.39	2.040
159.86	13.68	300.89	16.90	39.70	2.299	45.08	2.948
170.11	14.10	311.37	17.02	44.52	2.877	49.61	3.532
180.31	14.48	321.80	17.15	49.34	3.497	54.69	4.198
190.61	14.80	332.15	17.26	54.84	4.218	60.60	4.988
201.02	15.10	342.46	17.32	60.14	4.920		
				Molybdenum ditelluride (MoTe₂)			
Series I		Series II		263.08	17.99	11.14	0.328
56.99	7.533	178.23	16.33	273.12	18.09	12.35	0.421
63.40	8.497	189.16	16.60	283.09	18.20	13.70	0.552
70.65	9.442	199.92	16.85	293.00	18.32	15.28	0.714
79.98	10.56	210.53	17.06	302.87	18.42	17.28	0.934
89.63	11.58	221.02	17.28	312.68	18.53	19.57	1.223
99.10	12.37	231.40	17.48	322.72	18.67 [a]	21.91	1.553
109.86	13.17	241.68	17.64	332.98	18.78 [a]	24.31	1.920
121.26	13.93	251.87	17.78	343.50	18.84	26.90	2.346
132.08	14.55					29.93	2.871
142.49	15.06					33.63	3.534
152.94	15.51			Series IV		37.65	4.260
163.70	15.88	Series III		5.27	0.021	41.83	4.991
174.78	16.22	222.14	17.29	7.60	0.095	46.37	5.792
185.96	16.51	232.51	17.48	8.14	0.145	51.75	6.700
196.96	16.77	242.79	17.66	9.14	0.182	57.95	7.687
207.80	17.02	252.97	17.83	10.06	0.256		

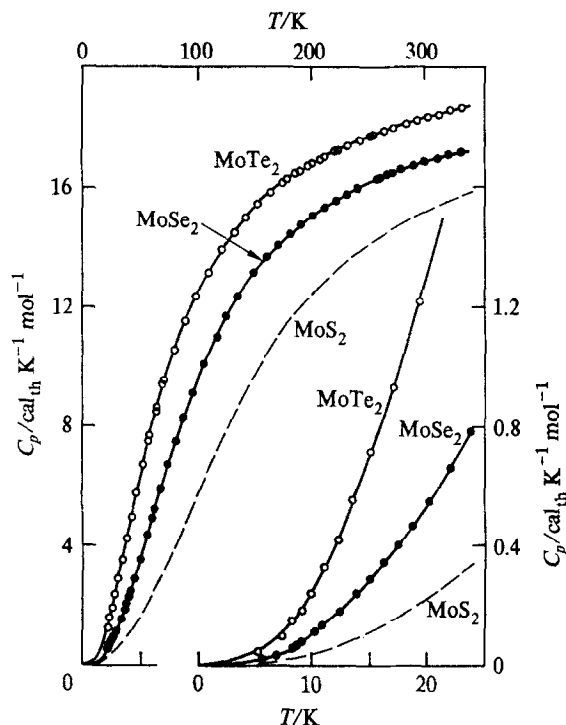[a] These points were given less weight in fitting smooth curves.

FIGURE 2. Molar heat capacities for MoS_2 (from reference 1) $MoSe_2$, and $MoTe_2$. For this series of isostructural chalcogenides, the Mo cation has an atomic weight of 95.94; that of the anion varies from 32.06 for sulfur, to 78.96 for selenium, and to 127.60 for tellurium.

approximates proportionality to T^2 is found, but this region clearly gives way to a T^3 behavior as lower temperatures are approached.

Some observers insist that an inflexion exists between the T^2-region and the T^3-region of the logarithmic plots (shown in figure 3). Literature assertions for the existence of a T^2-limiting law for heat capacity have either been heavily based on theory, on experimental results of less than adequate quality, or on failure to extend the experimental results to sufficiently low temperatures to encounter the region of T^3 dependence. As has already been noted, the tendency of plotting C_p against T^2 so minimizes the region of approach to $T \to 0$ that the authors are readily deluded toward erroneous conclusions.

So despite literature claims to the contrary, it has been shown that even for lamellar (sandwich-layer) molybdenum disulfide[1] when measurements are made to temperatures as low as 5 K, the T^2-proposal of Tarassov and others [9-12] for the limiting law fails as lower temperatures are approached. This is in contrast with claims made on measurements which did not extend below 18 K on MoS_2 and MoO_3.[13] The present investigations on the higher chalcogenides totally confirm the recent conclusions[1] and this further study establishes these conclusions as being independent of accidental atomic mass ratios, $etc.$ The same trends in heat capacity behavior

TABLE 3. Thermodynamic functions of molybdenum diselenide

$$(\text{cal}_{th} = 4.184 \text{ J})$$

$\dfrac{T}{\text{K}}$	$\dfrac{C_p}{\text{cal}_{th}\,\text{K}^{-1}\,\text{mol}^{-1}}$	$\dfrac{\{S^\circ(T) - S^\circ(0)\}}{\text{cal}_{th}\,\text{K}^{-1}\,\text{mol}^{-1}}$	$\dfrac{\{H^\circ(T) - H^\circ(0)\}}{\text{cal}_{th}\,\text{mol}^{-1}}$	$\dfrac{-\{G^\circ(T) - H^\circ(0)\}/T}{\text{cal}_{th}\,\text{K}^{-1}\,\text{mol}^{-1}}$
5	0.0233	0.0078	0.0293	0.0020
10	0.1002	0.0362	0.2563	0.0106
15	0.2827	0.110	1.191	0.0301
20	0.5244	0.222	3.179	0.0633
25	0.8518	0.373	6.579	0.110
30	1.275	0.564	11.857	0.169
35	1.777	0.797	19.457	0.241
40	2.336	1.070	29.718	0.328
45	2.939	1.380	42.889	0.427
50	3.580	1.723	59.173	0.539
60	4.909	2.493	101.60	0.799
70	6.212	3.348	157.25	1.101
80	7.444	4.259	225.61	1.439
90	8.577	5.202	305.81	1.804
100	9.600	6.160	396.79	2.192
110	10.51	7.118	497.43	2.596
120	11.31	8.068	606.63	3.013
130	12.02	9.002	723.37	3.437
140	12.64	9.916	846.72	3.868
150	13.18	10.81	975.88	4.301
160	13.66	11.67	1110.1	4.735
170	14.08	12.51	1248.9	5.168
180	14.46	13.33	1391.6	5.598
190	14.79	14.12	1537.9	6.026
200	15.09	14.89	1687.3	6.450
210	15.35	15.63	1839.6	6.870
220	15.59	16.35	1994.3	7.284
230	15.81	17.05	2151.3	7.694
240	16.00	17.72	2310.4	8.098
250	16.17	18.38	2471.2	8.496
260	16.33	19.02	2633.8	8.888
270	16.48	19.64	2797.9	9.275
280	16.63	20.24	2963.4	9.656
290	16.76	20.83	3130.4	10.031
300	16.89	21.40	3298.6	10.400
310	17.02	21.95	3468.2	10.764
320	17.13	22.49	3639.0	11.122
330	17.23	23.02	3810.8	11.475
340	17.31	23.54	3983.5	11.822
350	17.34	24.04	4156.8	12.164
273.15	16.53	19.83	2849.9	9.396
298.15	16.87	21.29	3267.4	10.332

TABLE 4. Thermodynamic functions of molybdenum ditelluride

$(cal_{th} = 4.184$ J)

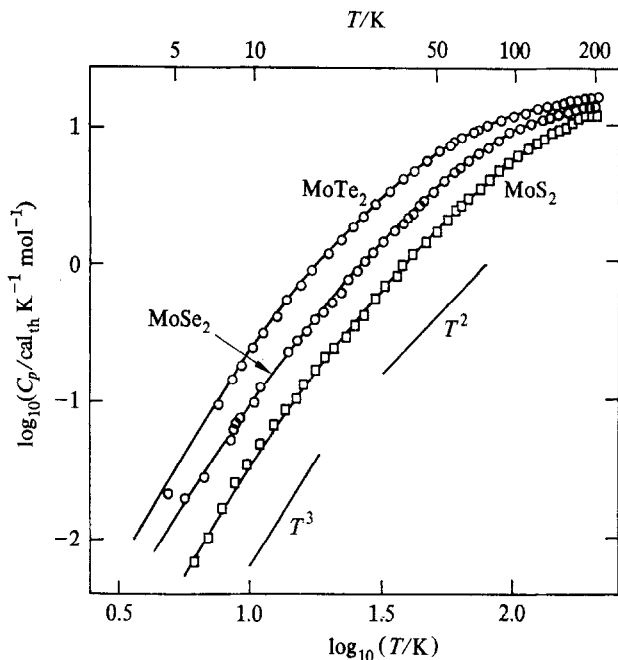| $\frac{T}{\text{K}}$	$\frac{C_p}{\text{cal}_{th}\,\text{K}^{-1}\,\text{mol}^{-1}}$	$\frac{\{S°(T) - S°(0)\}}{\text{cal}_{th}\,\text{K}^{-1}\,\text{mol}^{-1}}$	$\frac{\{H°(T) - H°(0)\}}{\text{cal}_{th}\,\text{mol}^{-1}}$	$\frac{-\{G°(T) - H°(0)\}/T}{\text{cal}_{th}\,\text{K}^{-1}\,\text{mol}^{-1}}$
5	0.0176	0.0060	0.0225	0.0015
10	0.244	0.0708	0.554	0.0154
15	0.681	0.247	2.797	0.0602
20	1.281	0.521	7.635	0.139
25	2.031	0.885	15.859	0.251
30	2.883	1.329	28.113	0.392
35	3.774	1.840	44.740	0.562
40	4.676	2.403	65.866	0.756
45	5.562	3.005	91.471	0.973
50	6.416	3.636	121.43	1.207
60	7.992	4.948	193.63	1.721
70	9.370	6.286	280.61	2.277
80	10.56	7.617	380.40	2.862
90	11.58	8.920	491.20	3.463
100	12.45	10.19	611.46	4.072
110	13.21	11.41	739.88	4.684
120	13.87	12.59	875.37	5.294
130	14.44	13.72	1017.0	5.899
140	14.94	14.81	1164.0	6.497
150	15.37	15.86	1315.6	7.086
160	15.75	16.86	1471.2	7.666
170	16.07	17.83	1630.3	8.235
180	16.36	18.75	1792.6	8.794
190	16.62	19.64	1957.5	9.342
200	16.85	20.50	2124.9	9.879
210	17.07	21.33	2294.5	10.404
220	17.26	22.13	2466.1	10.919
230	17.44	22.90	2639.6	11.423
240	17.61	23.65	2814.9	11.917
250	17.77	24.37	2991.9	12.401
260	17.92	25.07	3170.3	12.875
270	18.05	25.75	3350.1	13.339
280	18.17	26.41	3531.3	13.794
290	18.29	27.05	3713.6	14.240
300	18.40	27.67	3897.1	14.677
310	18.51	28.27	4081.6	15.106
320	18.61	28.86	4267.3	15.527
330	18.70	29.44	4453.9	15.940
340	18.79	30.00	4641.3	16.345
350	18.87	30.54	4829.6	16.743
273.15	18.09	25.96	3407.0	13.483
298.15	18.38	27.55	3863.0	14.597

FIGURE 3. Plot of $\log_{10}C_p$ against $\log_{10}T$ for MoS_2, $MoSe_2$, and $MoTe_2$.

with increasing temperature from T^3 through T^2 toward T^1 and perhaps nearly to T^0 behavior are to be expected to obtain generally. Hence, Newells' theoretical analysis[14] is substantially correct.

For material related to the structures, physical properties, and related details on MoS_2 and $MoTe_2$ supplementary material deposited elsewhere[15] may be consulted.

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15. For supplementary material including adjuvant, structural and physical properties of the substances reported in this paper and derived thermodynamics of chemical reactions made possible by the new data order NAPS document No. 02546 for 45 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number. Make checks payable to Microfiche Publications. Photocopies are $7.25. Microfiche are $1.50. Outside of the U.S. or Canada, postage is $2.00 for a PC or $0.50 for a fiche.