

Low-temperature heat capacity of anisotropic crystals Lamellar molybdenum disulfide

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Heat capacities of natural molybdenite crystals were made to test the T^2 limiting law for the heat capacity of a lamellar lattice near $T \rightarrow 0$. The findings are at variance with those of Smith *et al.* and accord with theoretical studies of Newell in that the T^3 limiting law is upheld. The results also permit a more accurate evaluation of the thermodynamic functions: at 298.15 K $C_p(T)$, $S^\circ(T)$, and $-\{G^\circ(T) - H^\circ(0)\}/T$ are (15.19 ± 0.03) , (14.96 ± 0.02) , and (6.475 ± 0.03) cal_{th} K⁻¹ mol⁻¹.

1. Introduction

Despite the fact that a preliminary publication and an oral presentation of this study had been made⁽¹⁾ and a conclusion that the $C_V = aT^2$ limiting law near $T \rightarrow 0$ was invalid, Smith *et al.*⁽²⁾ published the result of their investigation of MoS₂ and reached a conclusion contrary to ours; we present these results—somewhat belatedly—to set the record straight for MoS₂. A parallel situation indeed exists for the graphite-structured BN crystal⁽³⁾ and has similarly been rectified.^(1,4)

At the time this investigation was initiated, low-temperature heat-capacity measurements on molybdenum disulfide had been made only above 56 K by Anderson,⁽⁵⁾ a temperature too high to test the claim that the heat capacity of highly anisotropic lamellar structures obey a T^2 limiting law in contrast to the usual Debye T^3 limiting law⁽⁶⁾ for isotropic or very nearly isotropic crystals.

Two principal types of lamellar structures (composed of infinite sheets of atoms separated by interplanar distances greater than intratomic distances) are the graphite type (*e.g.* graphite and boron nitride), and the lamellar sandwich-type (of which MoS₂ is a variant usually designated the MoS₂ or C₇ type⁽⁷⁾). This structure is similar to the CdI₂ and CdCl₂ types except that the negatively charged atoms in MoS₂ are somewhat distorted out of closest packing; the difference has been attributed to increased polarization. A consequence is a more covalent and less ionic bonding than in CdI₂ or CdCl₂ types. Molybdenite (mineralogically occurring MoS₂) is indeed “layer-like” in certain macroscopic properties; for example, in the tendency to form crystal flakes, and in the ability to act as a good lubricant, like graphite,

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because of the ease with which the weakly bonded layers can glide over one another. A major difference between the graphite and the sandwich-type of structures is that in the latter the only contact between the electrically neutral layers is between like anions leading to weaker van der Waals forces between layers than within layers.

Most of the theoretical work on the low-temperature dependence of heat capacity of sandwich-type layer structures was based on graphite which is presumed to be represented by a $C_V = aT^2$ limiting law⁽⁸⁻¹¹⁾ although in some more recent cases a suggestion was made that at very low temperatures the heat capacity behavior might approach the usual Debye limiting law $C_V = bT^3$.⁽¹²⁻¹⁴⁾

Tarasov asserted that his formulas are applicable to a wide degree of anisotropy, ranging as far as non-interacting layers or chains to effectively three-dimensional structures in which the binding between layers or chains is as strong as within them. He gives as examples of sandwich-type structures $MnCl_2$, $FeCl_2$, *etc.*, and the intermediate type structures as $Mg(OH)_2$, $Cd(OH)_2$, *etc.* (*e.g.* compare references 15 to 18). Although he had claimed that heat capacities of layer and chain type structures agree well with theory, this seems to be a dubious claim, since most of the data were either of very low quality (performed by investigators other than himself) or taken only above 50 K, where neither limiting law can be expected to hold rigorously.

2. Experimental

CRYOGENIC APPARATUS

The Mark I Cryostat is an improved version of one depicted and described by Westrum, Hatcher, and Osborne⁽¹⁹⁾ as subsequently modified.⁽²⁰⁾

CALORIMETER

The gold-plated copper calorimeter (Laboratory designation W-5) was 3.8 cm in diameter and 7.7 cm in length with a wall thickness of 0.4 mm and is similar to one previously described.⁽²¹⁾ It contained eight vanes of 0.08 mm copper foil soldered to the central well and in spring contact with the cylindrical shell. An axial re-entrant well contained a capsule-type platinum thermometer within a cylindrical copper heater tube carrying 160 Ω of 0.08 mm diameter Advance fiber-glass-insulated wire wound bifilarly in double threaded grooves and cemented in place with Formvar. All thermometer and heater lead wires were brought to temperature equilibrium by cementing them with Formvar to a small copper spool held in place over the well with small cap screws. A small tube was soldered to the side of calorimeter for the differential thermocouple. Weighed amounts of Lubriseal grease were used to establish thermal contact between the thermometer, heater, spool, thermocouple, and calorimeter. After weighing the sample into the calorimeter and sealing the cover in place with Cerroseal solder (50 per cent by mass each of Sn and In, melting temperature 390 K) the calorimeter was evacuated and helium was admitted through a small hole drilled in the top of a thin-wall Monel stud. Pure helium gas was added at atmospheric pressure to provide thermal conductivity and the hole was then sealed with Cerroseal solder. The total amount of solder on the calorimeter was carefully adjusted to be the same as that during the heat-capacity determination on

the empty calorimeter. Together with thermometer, heater, spool and grease, the total mass of the calorimeter was 82.0 g.

The resistance thermometer was calibrated by the National Bureau of Standards from 10 to 350 K. Between 4 and 10 K we established a provisional temperature scale. It is believed that this temperature scale, IPTS-48, agrees with the thermodynamic scale within 0.1 K from 4 to 14 K within 0.03 K from 14 to 90 K and within 0.05 K from 90 to 373 K. Large metallic-lustered crystalline laminae of natural molybdenite from Lyndock Township, Ontario, Canada were cut into 1 cm squares. To remove inclusions of ferric molybdate and silicates, these 1 mm thick squares were leached for 30 h at 353 K in 3 mol dm⁻³ HCl with frequent changes of acid, until further HCl leaches yielded no thiocyanate test for iron. Preliminary analysis at this point indicated that the sample still contained 5 to 6 mass per cent of siliceous material. Two subsequent leachings with 48 mass per cent aqueous HF acid at near boiling temperatures for 24 h periods and several washes were followed by evacuation under high vacuum. Molybdenum was determined by the α -benzoinoxime method described by Hillebrand and Lundell.⁽²²⁾ Sulfur was determined by dissolution of molybdenite in concentrated HNO₃, evaporating to near dryness with HCl twice, filtration of any gangue present, adjustment of the solution to 0.05 mol dm⁻³ acidity, and removing molybdenum with a mercury cathode cell. Sulfur was then precipitated and weighed as barium sulfate.⁽²³⁾ AgNO₃ was used to test for chloride; and zirconium alizarinate was used to test for fluoride, as described by Feigl,⁽²⁴⁾ to ascertain that leaching agents were removed. An analysis was made for carbon (because of the possibility of graphite inclusions in the sample) by measuring carbon dioxide evolution upon oxidation of molybdenite in a gas analysis train. Light-gray material insoluble in the concentrated HNO₃ used in dissolving molybdenite for the other analyses is reported as insoluble residue. The analytical results indicated (59.85 ± 0.15) mass per cent Mo, (40.3 ± 0.2) mass per cent S, (0.0 ± 0.1) mass per cent C, 0.1 mass per cent insoluble residue, no Cl or F (theoretical: 59.94 mass per cent Mo and 40.06 mass per cent S). The mass of the calorimetric sample was 146.129 g.

3. Results

The experimental heat capacities corrected for curvature are presented in table 1 in chronological sequence, while the derived thermodynamic functions and smoothed values of the heat capacity are presented in table 2. Figure 1 shows the deviation between some earlier measurements of the heat capacity of molybdenum disulfide made by Anderson⁽⁵⁾ and by Smith *et al.*,⁽²⁾ and our results. Anderson's points scatter rather widely, and his data are—on the average—several per cent higher than those of this research. This may be due to the 0.84 mass per cent impurities contained in Anderson's sample for which corrections were estimated.

4. Discussion

An attempt to fit our low-temperature heat capacities for molybdenite to an expression of the form $C_p = aT^n$ is illustrated in figure 2, where the logarithm of the heat

TABLE 1. Heat capacity of molybdenum disulfide
(cal_{th} = 4.184 J)

T K	C_p cal _{th} K ⁻¹ mol ⁻¹	T K	C_p cal _{th} K ⁻¹ mol ⁻¹	T K	C_p cal _{th} K ⁻¹ mol ⁻¹	T K	C_p cal _{th} K ⁻¹ mol ⁻¹
Series I		184.21	11.67	335.58	15.81	20.82	0.239
62.80	2.597	193.47	12.12	345.67	15.97	22.79	0.298
68.23	3.020	202.89	12.51			24.86	0.362
74.32	3.512	212.34	12.88	Series II		26.93	0.435
80.93	4.079	216.29	13.03	5.74	0.0058	29.24	0.526
88.29	4.729	226.04	13.38	6.92	0.0099	32.21	0.655
96.01	5.404	235.80	13.69	7.87	0.0156	35.64	0.820
104.35	6.124	245.46	13.99	8.88	0.0238	38.52	0.972
112.93	6.860	255.14	14.25	9.89	0.0344	42.21	1.180
121.24	7.553	264.98	14.50	10.98	0.0475	46.30	1.433
129.59	8.221	274.92	14.72	12.20	0.0645	50.77	1.725
138.08	8.865	284.89	14.95	13.51	0.0841	55.51	2.055
146.77	9.482	294.94	15.11	14.80	0.106	60.86	2.457
155.99	10.09	305.13	15.31	16.12	0.130	60.84	2.439
165.33	10.66	315.29	15.50	17.55	0.159		
174.75	11.19	325.43	15.66	19.13	0.196		

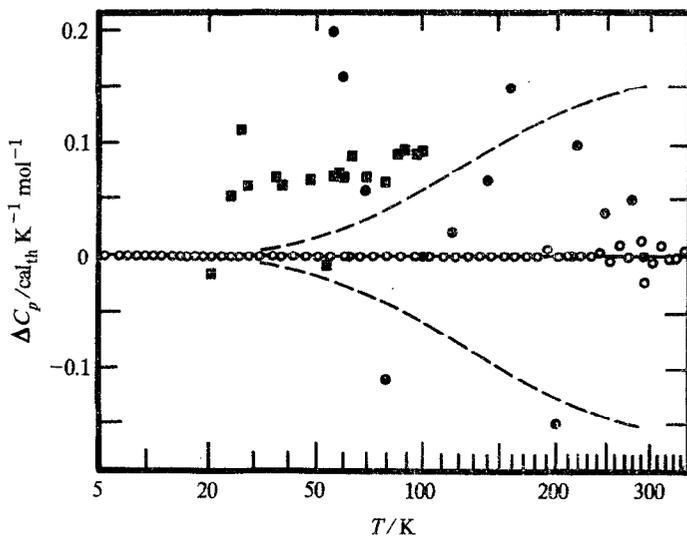
FIGURE 1. Deviation of the experimental heat capacities of MoS₂ from the smoothed curve for: ○, this research; ●, Anderson;⁽⁵⁾ ■, Smith *et al.*⁽²⁾ The dashed lines indicate ±1 per cent deviation.

TABLE 2. Thermodynamic functions of molybdenum disulfide
(cal_{th} = 4.184 J)

$\frac{T}{K}$	C_p cal _{th} K ⁻¹ mol ⁻¹	$\{S^\circ(T) - S^\circ(0)\}$ cal _{th} K ⁻¹ mol ⁻¹	$\{H^\circ(T) - H^\circ(0)\}$ cal _{th} mol ⁻¹	$-\{G^\circ(T) - H^\circ(0)\}/T$ cal _{th} K ⁻¹ mol ⁻¹
10	0.036	0.012	0.089	0.003
15	0.109	0.039	0.439	0.010
20	0.218	0.084	1.237	0.022
25	0.366	0.148	2.69	0.040
30	0.558	0.231	4.98	0.065
35	0.798	0.334	8.33	0.096
40	1.052	0.457	12.92	0.134
45	1.352	0.597	18.92	0.177
50	1.673	0.758	26.48	0.228
60	2.389	1.125	46.71	0.346
70	3.163	1.549	74.32	0.487
80	3.999	2.024	110.01	0.649
90	4.880	2.546	154.40	0.830
100	5.748	3.105	207.56	1.029
110	6.612	3.693	269.38	1.244
120	7.452	4.305	339.71	1.474
130	8.254	4.933	418.3	1.716
140	9.002	5.572	504.6	1.968
150	9.697	6.218	598.1	2.231
160	10.34	6.864	698.3	2.500
170	10.93	7.509	804.7	2.776
180	11.47	8.150	916.7	3.057
190	11.96	8.782	1033.9	3.341
200	12.39	9.407	1155.6	3.629
210	12.79	10.022	1281.6	3.919
220	13.16	10.625	1411.4	4.210
230	13.51	11.219	1544.7	4.503
240	13.67	11.799	1681.4	4.793
250	14.22	12.369	1821.1	5.084
260	14.38	12.928	1963.6	5.376
270	14.62	13.475	2108.6	5.665
280	14.83	14.011	2255.9	5.954
290	15.03	14.535	2405.2	6.241
300	15.22	15.048	2556.5	6.526
350	16.03	17.457	2947.6	9.035
273.16	14.69	13.646	2154.9	5.757
298.16	15.19	14.955	2528.5	6.475

capacity is plotted against the logarithm of the temperature. Such a plot should yield a straight line, of slope n , over any temperature range in which $C_p = aT^n$ (where a and n are constants) fits the experimental results well. It is clear that the plot is not a straight line but has curvature throughout the entire temperature range illustrated. The solid straight line, which has a slope of 2.0 can be seen to approximate the true

curve within about 1 per cent from about 40 to 60 K, but it is obvious that even in this range the experimental curve varies systematically from a straight line, and that a straight line is a good approximation to the curve, only as a chord or a tangent. The dashed line indicates a slope of 3.0 which does approximate the experimental curve at the lowest temperatures measured.

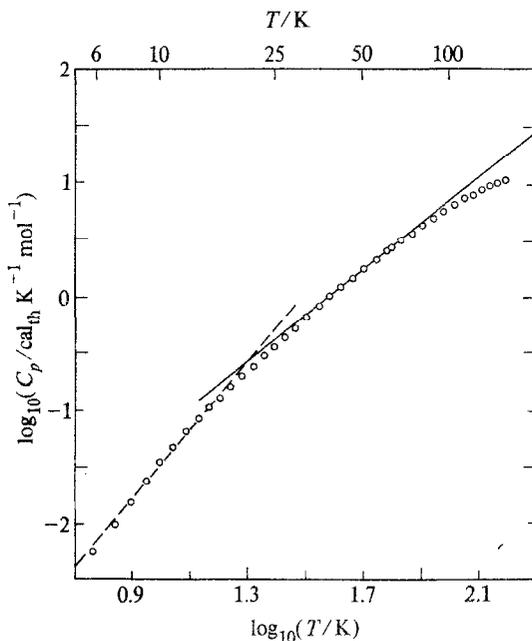


FIGURE 2. Logarithm of the heat capacity of MoS_2 plotted against the logarithm of temperature. The dashed line represents $C_p \propto T^3$, the solid line $C_p \propto T^2$.

That the slope of such a log-log plot be regarded as the exponent in a heat-capacity function of the form $C_p = aT^n$ is valid only for a linear curve. Suppose that the heat capacity is represented by a polynomial of the form

$$C_p = \sum_{n=0}^m a_n T^n, \quad (1)$$

in which n can assume integral or non-integral values. The degree of the polynomial (*i.e.* the highest exponent in T) is not necessarily the dominant term, but the contribution of this term may, in fact, be insignificant except at the highest temperatures since the coefficient for this term may be quite small. Provided the heat capacity may be adequately represented by a polynomial having only *positive* coefficients, a different interpretation of the slope $d \log C_p / d \log T$ may be given. Differentiation of equation (1) with respect to temperature yields:

$$dC_p/dT = \sum_{n=1}^m n a_n T^{n-1}. \quad (2)$$

Multiplying both sides of (2) by T/C_p gives:

$$(T/C_p)dC_p/dT = \sum_{n=1}^m na_n T^{n-1}(T/C_p),$$

and

$$W = (T/C_p)dC_p/dT = \sum_{n=1}^m na_n T^n/C_p. \quad (3)$$

Here, it will be seen that W is a weighted average of *all exponents* with respect to the contribution of each term to the total heat capacity at a given temperature. Equation (3) can then be converted to

$$W = d \log C_p/d \log T.$$

Hence, the slope of a log-log plot may be considered as a weighted average of exponents under the constraint of positive coefficients. The fundamental property of this weighted average is that it will increase as a function of temperature between the limits of the lowest and highest exponents in the polynomial. This means that in a log-log plot of heat capacities, the slope at a given temperature may be interpreted as a weighted average of exponents *only* if this slope is increasing. In the region of validity for W , if W rises above a certain integral value, n , then the polynomial requires at least one term of degree greater than n . Above the temperature at which the slope begins to depart from linearity its interpretation as a weighted average is not valid, since the decrease in slope implies that *negative* coefficients must be used in the polynomial fit to C_p .

In summary, despite literature claims to the contrary on MoS_2 and MoO_3 ,⁽¹⁾ we have shown that even for lamellar (sandwich-layer) molybdenum disulfide the T^2 proposal of Tarassov and others^(8-11, 16-18) as 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. Another investigation from this laboratory on the higher molybdenum chalcogenides⁽²⁵⁾ confirms these conclusions and establishes them as independent of fortuitous atomic mass ratios, *etc.* The same trends in heat capacity behavior with increasing temperature from T^3 through T^2 toward T^1 and perhaps nearly to T^0 behavior are expected to obtain generally. Hence, Newell's theoretical analysis^(26, 27) is substantially correct.

Fredrickson and Chasanov⁽²⁸⁾ have measured the enthalpy (relative to 298.15 K) of hexagonal MoS_2 in the temperature range of 500 to 1200 K, by drop calorimetry. Using fluorine bomb calorimetry, O'Hare *et al.*⁽²⁹⁾ determined:

$$\Delta H_f^\circ(\text{MoS}_2, c, 298.15 \text{ K}) = -(65.8 \pm 1.2) \text{ kcal}_{\text{th}} \text{ mol}^{-1},$$

and combining this value with $S^\circ(298.15 \text{ K})$ for Mo and $S^\circ(\text{rhombic}, 298.15 \text{ K})$ and the $S^\circ(298.15 \text{ K})$ of $\text{MoS}_2(c)$ from this research yields

$$\Delta G_f^\circ(\text{MoS}_2, c, 298.15 \text{ K}) = -(63.7 \pm 1.2) \text{ kcal}_{\text{th}} \text{ mol}^{-1}.$$

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