

Manganese Disulfide (Hauerite) and Manganese Ditelluride. Thermal Properties from 5 to 350°K and Antiferromagnetic Transitions*

EDGAR F. WESTRUM, JR.

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104

AND

FREDRIK GRØNVOLD

Institute of Inorganic Chemistry, University of Oslo, Blindern, Norway

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The heat capacities of manganese disulfide and manganese ditelluride were determined by adiabatic calorimetry in the range 5–350°K. Lambda-type transitions are present in both compounds with maxima at 47.93°K for MnS₂ and at 83.0°K for MnTe₂. Entropies, enthalpies, and Gibbs energy function values are calculated and tabulated. At 298.15°K they are: $S^\circ = 23.88$ cal/mole·°K, $H^\circ - H_0^\circ = 3384$ cal/mole, $-(G^\circ - H_0^\circ)/T = 12.258$ cal/mole·°K for MnS₂ and 34.66, 4416, and 19.847 for MnTe₂. The clearly cooperative entropy increments are only 0.71 cal/mole·°K for MnS₂ and 0.80 for MnTe₂. Available magnetic susceptibility data are interpreted in terms of zero-field splitting of the $^6S_{5/2}$ state of the manganese $3d^5$ electrons. The resulting contributions to the heat capacity are evaluated. At 298°K the combined λ -transitional and Schottky contributions to the entropy are 2.6 and 2.4 cal/mole·°K for MnS₂ and MnTe₂, respectively.

INTRODUCTION

Manganese disulfide, manganese ditelluride, and manganese diselenide all crystallize with pyrite-type structures^{1–3} in which manganese atoms and the center of the dichalcogenide groups form a sodium chlorideliike arrangement. The structure is primitive cubic since the axes of the four X_2 groups in the unit cell (symmetrical about 0, $\frac{1}{2}$, 0, etc.) are parallel to different body diagonals. Each manganese atom is octahedrally coordinated to six chalcogen atoms, while each chalcogen atom is tetrahedrally coordinated to three manganese and one chalcogen atom.

These paramagnetic compounds have five unpaired spins.^{3,4} Antiferromagnetic spin arrangements have been observed by neutron diffraction^{5,6} near 4°K. The ditelluride was found to exhibit an ordering of the first kind,⁷ in which each manganese atom has eight nearest metal neighbors with antiparallel spins and four with parallel spins, while all six second-nearest metal neighbors have spins parallel to the central atom. In the case of the disulfide, the ordering was found to be of the third kind,⁸ which differs from the first kind in the arrangement of the second-nearest neighbors, with only four of them having parallel spins.

The present study was undertaken to gain further insight into the magnetic order-disorder processes by exploring the shape and location of the expected heat capacity maxima. Furthermore, it was anticipated that resolutions of the magnetic contributions to the heat capacities and thermodynamic functions of these compounds would be possible.

EXPERIMENTAL

Samples

The manganese disulfide used was in the form of selected naturally occurring hauerite single crystals from Raddusa, Sicily. The crystals were carefully

abraded with fine emery paper on all faces to remove oxidation products. Chemical and spectrographic analyses were performed on several crystals. Duplicate chemical analyses by L. Reichen on one crystal indicated an average of 45.93% Mn and 53.65% S, corresponding to the formula MnS_{2.00}. Determinations on two other crystals by C. O. Ingamels indicated 46.46% Mn by weighing as Mn₂P₂O₇, 52.90% S by the fusion method, and 53.20% S by oxidation to elemental sulfur and sulfate. From these sulfur values, the composition of the sulfide would be deduced as MnS_{1.9}. Independent spectrographic analyses by W. H. Worthing and N. Suhr agreed on the presence of Sn (0.05%), Fe (0.03%), and Si (0.02% and 0.06%). In the sample further impurities found were as follows: V (0.03%), Ca (0.007%), Cr (0.002%), Mg (0.002%), Co (0.001%), Ni (0.001%), Nb (0.0007%), Ba (0.0003%), Mo (0.003%), and Ti (0.0003%). The following elements were also sought but not found: Ag, As, Au, B, Be, Bi, Cd, Ce, Ga, Ge, Hf, Hg, In, K, La, Li, Na, Pb, Pd, Pt, Re, Sb, Se, Sr, Ta, Te, Th, Tl, U, W, Y, Yb, and Zr. Se and Te were not detected by x-ray fluorescence.

The lattice constant determined on powdered specimens using a Guinier-type camera with KCl ($a_{20} = 6.2919$ Å) as an internal standard were $a = 6.102 \pm 0.001$ Å, which agrees well with earlier values⁹ (6.109 ± 0.005 Å*, 6.107 ± 0.003 Å,¹¹ 6.1008 ± 0.0001 Å at 29°C,¹² and 6.1016 Å at 20°C.¹³

The manganese ditelluride sample was prepared by reacting stoichiometric amounts of manganese and tellurium in an evacuated and sealed quartz tube. The 99.995% electrolytic manganese supplied by Light Ltd. was reported to contain the following impurities (in ppm): Cu < 1, Mg < 5, Si < 5. After pickling the metal with 5% nitric acid in ethyl alcohol, it was degassed *in vacuo* at 600°C for 2 h. The 99.999% tellurium from the American Smelting and Refining

Co. contained no impurities detectable by spectrographic methods. The manganese-tellurium mixture was heated at 800°C for two days in a double-walled tube and, after cooling to room temperature, the telluride separated from the shattered inner tube. The crushed sample was then annealed at 500°C for one week and cooled with the furnace. Chemical analyses of manganese and tellurium indicated 18.35% manganese and 82.05% tellurium, which corresponds to a composition $MnTe_{1.92}$ for the telluride. The amount of SiO_2 present in the sample was found to be 0.17%. The lattice constant of the ditelluride was determined to be $a = 6.954 \pm 0.001 \text{ \AA}$, in good agreement with three earlier results ($6.957 \pm 0.002 \text{ \AA}$,² $6.951 \pm 0.002 \text{ \AA}$,¹⁴ and 6.958 \AA ¹⁵).

Cryogenic Technique

The heat capacities were measured in the Mark II cryostat¹⁶ with intermittent heating of the sample under quasiadiabatic conditions. The gold-plated copper calorimeter (laboratory designation W-31) with a capacity of 48 cm^3 was surrounded by adiabatic shields provided with electronic control. These consisted of three separate channels of recording circuitry with proportional, rate, and reset actions. Temperature differences between calorimeter and shields were maintained within a millidegree, and thereby the heat exchange was reduced to a magnitude negligible compared with other sources of error. The heat capacity of the calorimeter-heater-thermometer assembly was determined in a separate series of experiments. Small corrections were applied for the differences in the amounts of indium-tin solder for sealing the calorimeter, Apiezon-T grease for thermal contact between calorimeter and heater-thermometer assembly, and helium of about 10 cm Hg pressure for improving thermal equilibration between calorimeter and sample. Temperatures determined with the strain-free platinum resistor (laboratory designation A-5) are considered to accord with the thermodynamic temperature scale to within 0.03°K . All measurements of mass, temperature, resistance,

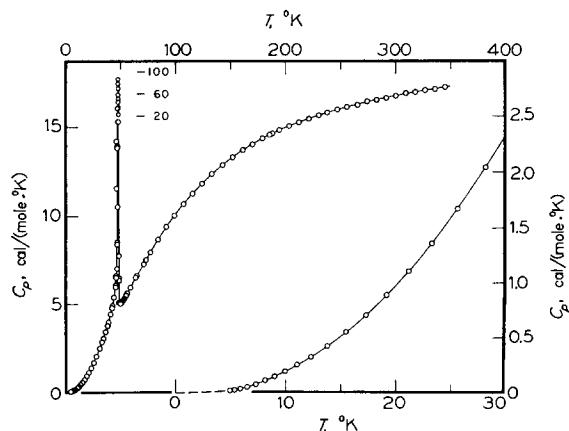


FIG. 1. Heat capacity of MnS_2 (hauerite).

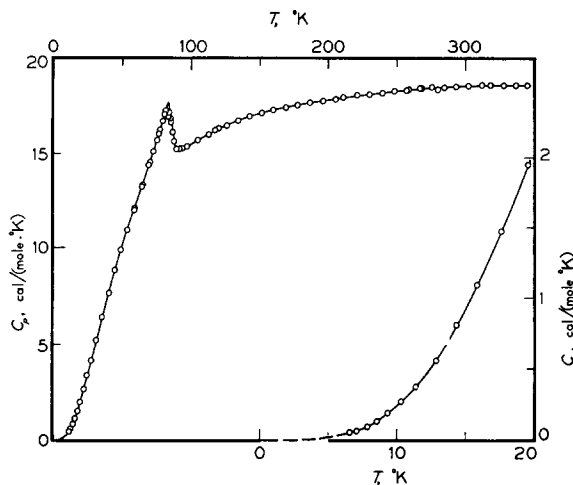


FIG. 2. Heat capacity of $MnTe_2$.

voltage, and time are based upon calibrations or standardizations performed by the U.S. National Bureau of Standards.

RESULTS AND DISCUSSION

The experimental heat capacity values for manganese disulfide (hauerite) and manganese ditelluride are listed in Table I in chronological sequence at the mean temperatures of the measurements. The data have been corrected for curvature of the heat capacity curve and are given in terms of the defined thermochemical calorie, equal to 4.1840 J, and an ice point of 273.15°K . The probable errors in the measurements are considered to decrease from about 3% at 5°K to 0.5% at 10°K and to less than 0.1% above 20°K .

In both compounds, λ -type maxima in the heat capacities were observed, the one in hauerite rising rather sharply to a maximum of $87.26 \text{ cal/mole}\cdot^\circ\text{K}$ over a 0.04°K interval at 47.93°K , and the one in manganese ditelluride to a less pronounced maximum of $17.52 \text{ cal/mole}\cdot^\circ\text{K}$ at 83.0°K . These anomalies are shown in Figs. 1 and 2.

The smoothed heat capacities and thermodynamic functions derived from them by means of a digital computer using a previously described program¹⁷ are given in Table II for selected temperatures. The thermodynamic functions may be considered reliable to better than 0.1% above 100°K .

Enthalpy-type determinations (ΔH Run E, 80 – 113°K , and ΔH Run F, 113 – 181°K on MnS_2 ; ΔH Run A, 54 – 93°K , and ΔH Run B, 120 – 208°K on $MnTe_2$) noted in Table I provide a test of the heat capacity measurement and integration procedures. The enthalpy increments thus determined accord with corresponding values derived from the smoothed heat capacity curves well within $\pm 0.1\%$.

In order to evaluate the energy associated with λ -type transitions in MnS_2 the Debye θ 's calculated from the experimental heat capacities at constant pressure were

TABLE I. Heat capacity of manganese disulfide (hauerite) and manganese ditelluride.^a

<i>T</i>	<i>C_p</i>	<i>T</i>	<i>C_p</i>	<i>T</i>	<i>C_p</i>	<i>T</i>	<i>C_p</i>
Manganese disulfide MnS ₂ (hauerite); 1 mole = 119.07 g							
Series I		15.53	0.555	46.62	6.612	51.40	5.127
64.99	6.653	17.34	0.709	47.01	7.055	52.41	5.248
71.05	7.318	19.21	0.891	47.36	8.474	53.40	5.324
77.40	8.001	21.20	1.107	47.63	14.114	55.28	5.533
84.23	8.725	23.32	1.364	47.77	34.74	59.23	5.985
91.59	9.419	25.63	1.673	47.84	78.14	64.43	6.590
99.39	10.074	28.20	2.043	47.90	87.00	73.39	7.574
107.43	10.707	31.08	2.496	47.94	68.93		
115.56	11.291	34.38	3.066	48.00	37.32	Δ <i>H</i> Run E	
124.11	11.858	38.13	3.792	48.13	15.36		
133.33	12.409	42.43	4.829	48.51	6.511	Δ <i>H</i> Run F	
142.76	12.911	Δ <i>H</i> Run A				185.71	14.603
151.99	13.350	51.26	5.176	Series VI		194.63	14.862
161.13	13.741	56.34	5.657	46.57	6.586	203.52	15.09
170.15	14.076	Series III		47.43	10.537	212.49	15.31
179.18	14.399	33.13	2.850	47.81	58.08	221.55	15.51
188.20	14.683	36.32	3.432	47.89	86.88	230.59	15.70
Series II		39.09	3.993	47.93	87.26	238.09	15.85
4.98	0.020	41.02	4.435	47.97	45.65	247.24	16.02
5.38	0.024	42.77	4.905	48.06	23.73	256.32	16.17
5.88	0.035	44.36	5.419	48.41	7.771	265.30	16.29
6.54	0.051	Δ <i>H</i> Run B		Series VII		274.17	16.48
7.31	0.076	50.12	5.031	49.05	5.081	282.99	16.54
8.15	0.111	Series IV		Δ <i>H</i> Run D		291.75	16.67
9.04	0.154	42.77	4.905	49.58	4.992	300.49	16.77
9.99	0.205	Δ <i>H</i> Run C		50.11	5.045	309.27	16.92
11.05	0.255	Series V		50.63	5.059	318.11	17.00
12.32	0.324	45.71	6.024			327.03	17.08
13.82	0.427					336.11	17.15
						345.33	17.26
Manganese ditelluride, MnTe ₂ ; 1 mole = 310.16 g							
Series I		9.31	0.182	Series IV		96.88	15.40
257.01	18.39	10.29	0.265	58.75	12.114	104.66	15.73
268.21	18.48	11.40	0.370	64.36	13.370	112.46	16.05
278.97	18.47	12.85	0.558	69.11	14.391	120.05	16.34
Series II		14.36	0.805	72.60	15.16	Δ <i>H</i> Run B	
117.57	16.27	15.88	1.093	75.19	15.77	211.17	18.00
125.37	16.51	17.63	1.472	77.33	16.29	220.88	18.12
134.12	16.78	19.60	1.949	79.23	16.77	230.00	18.17
142.68	16.99	22.12	2.612	80.75	17.16	239.19	18.25
151.16	17.19	24.79	3.343	81.74	17.34	248.46	18.33
159.79	17.33	27.53	4.124	82.40	17.44	257.67	18.40
168.73	17.50	31.18	5.155	83.00	17.52	266.84	18.46
177.79	17.61	35.62	6.416	83.60	17.41	275.94	18.53
186.86	17.74	40.25	7.666	84.25	17.22	285.02	18.55
196.02	17.84	44.90	8.854	84.92	16.96	294.05	18.58
205.17	17.93	49.28	9.930	85.59	16.66	303.12	18.62
		53.66	10.955	86.28	16.11	312.27	18.65
		58.59	12.076	87.33	15.67		
Series III		64.07	13.296	89.47	15.23	Series VI	
6.58	0.041	70.03	14.587	93.92	15.27	318.84	18.64
7.05	0.059	76.46	16.08	Series V		328.12	18.64
7.85	0.088	83.46	16.98	Δ <i>H</i> Run A		337.37	18.67
8.52	0.124	91.55	15.29			345.80	18.67

^a Units: calorie, mole, degree Kelvin.

TABLE II. Thermodynamic properties of manganese disulfide (hauerite) and manganese ditelluride.^a

T	C_p	S°	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$	T	C_p	S°	$H^\circ - H_0^\circ$	$-(G^\circ - H_0^\circ)/T$
Manganese disulfide, MnS_2 (hauerite); 1 mole = 119.07 g					Manganese ditelluride, $MnTe_2$; 1 mole = 310.16 g				
5	0.018	0.006	0.02	0.002	5	0.019	0.006	0.023	0.002
10	0.196	0.063	0.48	0.015	10	0.228	0.060	0.471	0.013
15	0.513	0.198	2.20	0.051	15	0.918	0.266	3.126	0.058
20	0.975	0.405	5.85	0.112	20	2.041	0.676	10.382	0.157
25	1.584	0.685	12.19	0.198	25	3.403	1.275	23.94	0.318
30	2.322	1.037	21.90	0.307	30	4.829	2.022	44.52	0.538
35	3.182	1.458	35.61	0.441	35	6.233	2.872	72.19	0.810
40	4.195	1.947	53.97	0.598	40	7.600	3.794	106.79	1.125
60	6.079	4.572	183.5	1.514	45	8.879	4.765	148.05	1.475
70	7.212	5.595	250.0	2.024	50	10.099	5.764	195.5	1.854
80	8.276	6.629	327.5	2.535	60	12.391	7.810	308.1	2.675
90	9.251	7.661	415.2	3.047	70	14.588	9.886	443.0	3.557
100	10.129	8.682	512.2	3.560	80	16.97	11.984	600.5	4.476
110	10.912	9.684	617.5	4.071	90	15.21	14.053	766.2	5.540
120	11.607	10.664	730.1	4.580	100	15.54	15.667	919.4	6.473
130	12.222	11.618	849.4	5.085	110	15.96	17.169	1077.0	7.378
140	12.767	12.544	974.4	5.585	120	16.33	18.574	1238.5	8.253
150	13.251	13.442	1104.5	6.079	130	16.65	19.893	1403.4	9.098
160	13.684	14.311	1239.2	6.566	140	16.92	21.138	1571.3	9.914
170	14.070	15.153	1378.0	7.047	150	17.16	22.313	1741.8	10.702
180	14.418	15.967	1520.5	7.520	160	17.35	23.427	1914.3	11.462
190	14.730	16.755	1666.2	7.985	170	17.52	24.484	2088.7	12.198
200	15.01	17.518	1815.0	8.443	180	17.66	25.489	2264.6	12.908
210	15.26	18.256	1966.4	8.893	190	17.78	26.448	2441.8	13.596
220	15.49	18.972	2120.2	9.335	200	17.89	27.362	2620.1	14.262
230	15.70	19.665	2276.1	9.769	210	17.99	28.238	2799.5	14.906
240	15.89	20.337	2434.0	10.195	220	18.08	29.08	2979.9	15.53
250	16.06	20.989	2593.8	10.614	230	18.17	29.88	3161.1	16.14
260	16.22	21.622	2755.2	11.025	240	18.25	30.66	3343.2	16.73
270	16.37	22.237	2918.1	11.429	250	18.33	31.40	3526.1	17.30
280	16.51	22.835	3082.5	11.826	260	18.41	32.12	3709.8	17.86
290	16.65	23.416	3248.3	12.216	270	18.47	32.82	3894.2	18.40
300	16.77	23.983	3415.4	12.598	280	18.53	33.49	4079.2	18.92
310	16.89	24.535	3583.7	12.975	290	18.58	34.14	4264.8	19.44
320	17.01	25.073	3753.2	13.344	300	18.62	34.77	4450.8	19.94
330	17.11	25.598	3923.8	13.708	310	18.64	35.39	4637.1	20.43
340	17.20	26.110	4095.4	14.065	320	18.65	35.98	4823.5	20.90
350	17.28	26.610	4267.8	14.416	330	18.65	36.55	5010.0	21.37
273.15	16.41	22.43	2970	11.555	340	18.66	37.11	5196.6	21.82
298.15	16.75	23.88	3384	12.528	350	18.68	37.65	5383.2	22.27
					273.15	18.49	33.03	3952	18.565
					298.15	18.61	34.66	4416	19.847

^a Units: calorie, mole, degree Kelvin.

smoothly interpolated over the range 25–65°K and the noncooperative heat capacities calculated from them. By this procedure, the entropy and enthalpy of transition are found to be $\Delta S_t = 0.71$ cal/mole·°K and $\Delta H_t = 33$ cal/mole for MnS_2 (see Table III). For $MnTe_2$ a similar procedure over the range 54–93°K leads to

$\Delta S_t = 0.55$ cal/mole·°K and $\Delta H_t = 41$ cal/mole (see Table IV).

The estimated entropy values are only a fraction of the value $R \ln 6 = 3.56$ cal/mole·°K expected for randomization of the manganese $3d$ electrons over the state ${}^6S_{5/2}$ and indicate that some of the levels are

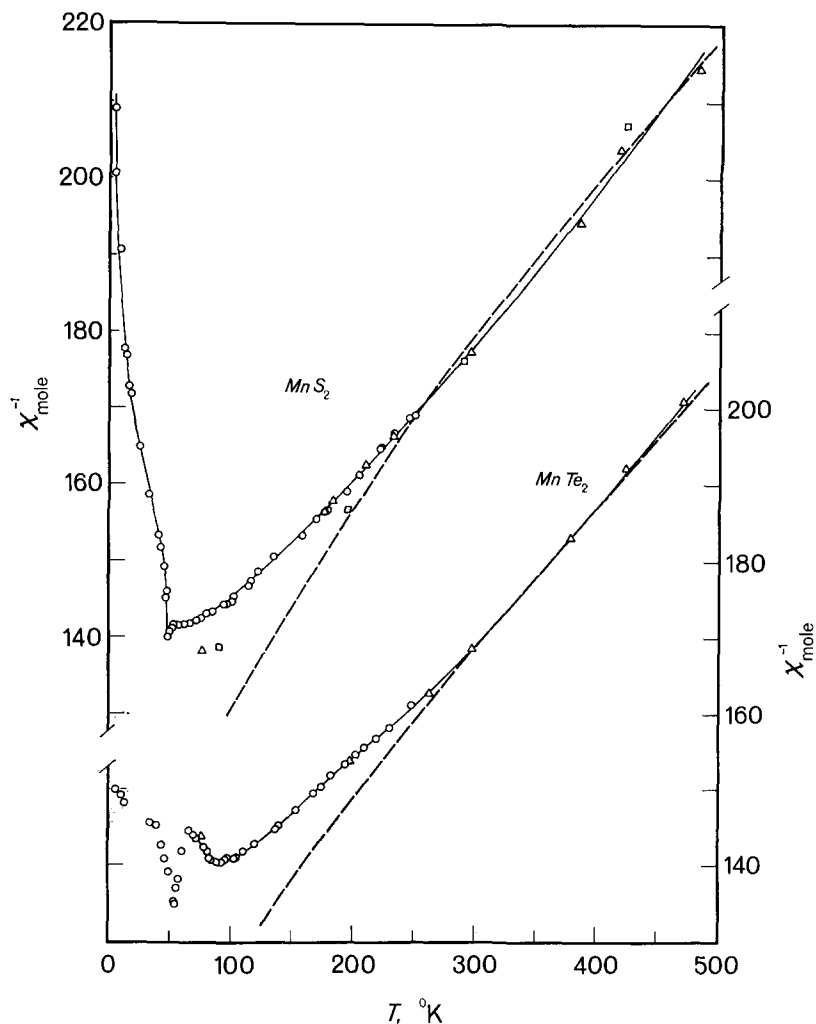


FIG. 3. Reciprocal molar susceptibilities of MnS_2 and MnTe_2 (corrected for diamagnetism) vs temperature. Δ represents data by Haraldsen and Klemm⁴; \square represents data by Hastings *et al.*⁵; \circ represents data by Lin¹⁸; — represents experimental data; --- represents calculated data assuming zero-field splitting as indicated in the text.

TABLE III. Enthalpy and entropy of transition of MnS_2 (hauerite).^a

Determinations designation	No. of determinations	T_1	T_2	$H_{T_2} - H_{T_1}$	$H_{65} - H_{44}$
MnS ₂ (hauerite)					
A (Series II)	2	44.737	53.968	72.226	81.84
B (Series III)	6	43.599	50.884	62.087	81.73
C (Series V)	1	46.098	48.785	37.460	82.05 ^b
Series V	12	44.988	48.806	44.045	81.70
Series VI	8	46.023	48.690	37.341	81.76
D (Series VII)	8	46.094	53.884	63.673	81.72
Average value				$H_{65}^\circ - H_{44}^\circ = 81.8$	
				$H_{44}^\circ - H_{25}^\circ = 60.6$	
				$H_{65}^\circ - H_{56}^\circ = 60.8$	
				$H_{65}^\circ - H_{25}^\circ = 203.2$	
Noncooperative contribution				$H_{65}^\circ - H_{25}^\circ = 170.4$	
				$\Delta H_t = 33$	
				$\Delta S_t = 0.71$	
$T_t = 47.93^\circ\text{K}$					

^a Units: caloric, mole, degree Kelvin.

^b Rejected from average by Chauvenet criterion.

TABLE IV. Enthalpy and entropy of transition of $MnTe_2$.^a

Determinations designation	No. of runs	T_1	T_2	$H_{T_2}-H_{T_1}$	$H_{95}-H_{55}$
Series III	7	51.339	95.958	647.02	592.6
Series IV	19	55.917	96.937	611.28	591.7
A	1	53.687	93.060	577.64	592.0
Average value				$H_{95}-H_{55}=592.1$	
Lattice contribution				$H_{95}-H_{55}=551$	
				$\Delta Ht=41$	
				$\Delta St=0.55$	

^a Units: calorie, mole, degree Kelvin.

occupied only at temperatures far above the transition. This interpretation is supported by the magnetic susceptibility measurements. Data for MnS_2 by Lin,¹⁸ Haraldsen and Klemm,⁴ and Hastings *et al.*⁵ show a Weiss constant of about 600°K which might be explained in terms of a large zero-field splitting of the $\pm\frac{3}{2}$ and especially of the $\pm\frac{5}{2}$ levels from the $\pm\frac{1}{2}$ levels. The observed molar susceptibility data can be fitted by the equation

$$\chi_{mole} = \frac{N\beta^2 g^2}{kT} \times \left[\frac{(\frac{1}{2})^2 + (\frac{3}{2})^2 \exp(-E_1/kT) + (\frac{5}{2})^2 \exp(-E_2/kT)}{1 + \exp(-E_1/kT) + \exp(-E_2/kT)} \right],$$

where E_1 and E_2 are the energy separations of the excited states from the ground state, N is Avogadro's

number, g is the Landé factor, β is the Bohr magneton, k is Boltzmann's constant, and T is the absolute temperature. As can be seen from Fig. 3, good agreement is obtained with $E_1/k=190^\circ\text{K}$ and $E_2/k=900^\circ\text{K}$. According to this picture, the λ -type transition should involve mainly the $\pm\frac{1}{2}$ states, since the higher ones are slightly populated at the transition temperature, and are not fully excited even at 298°K. At this temperature, the transitional entropy contribution is $R \ln 6$ minus that for the order persisting at 298°K, i.e.,

$$\Delta St = 3.56 - 0.60 = 2.96 \text{ cal/mole}\cdot^\circ\text{K}.$$

Separation of the magnetic heat capacity from that of the lattice presupposes knowledge about the phonon dispersion spectrum which, unfortunately, is not yet available. Direct comparison with the structurally related iron compounds is questionable because of the large influence of the number of unpaired 3d electrons on the metal-nonmetal bond distances (2.59 Å in hauerite and 2.27 Å in pyrite) and thus on the lattice heat capacity. An estimate of the lattice heat capacity can be obtained by subtracting the assumed Schottky contribution from the observed heat capacity in the region above 70°K (where the contribution of the λ -type transition presumably vanishes) and calculating θ_D 's for residual heat capacity. These are joined smoothly with those in the region 10–15°K to provide a lattice estimate over the anomalous region. With this tentative lattice contribution (see Fig. 4) a magnetic entropy increment ΔS at 298°K = 2.6 cal/mole·°K is obtained. Residual contributions from the λ -type transition above 70°K and antiferromagnetic spin waves below 15°K would tend to increase this value.

The relative sharpness of the heat capacity maximum in MnS_2 poses the question as to whether or not the transition is of first order. It might be answered by the Landau theory of phase transitions,¹⁹ which puts definite and quite restrictive conditions on the changes in symmetry allowed during a higher-order transition. Dimmock²⁰ has discussed these requirements for the magnetic transition in $MnSe_2$ and found that the low-temperature structure cannot transform con-

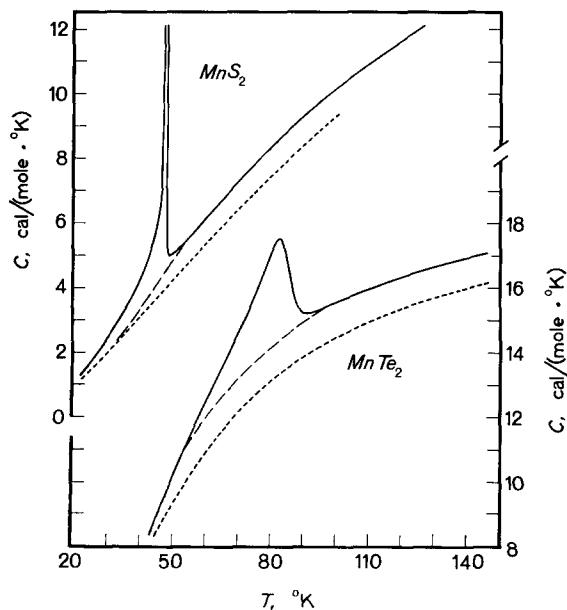


FIG. 4. Heat capacities of MnS_2 and $MnTe_2$ in the transition region. — represents experimental data; --- represents estimated lattice heat capacity; - - - represents lattice heat capacity plus Schottky contribution.

tinuously into the pyrite-type structure; for MnS_2 and MnTe_2 no such restrictions exist. However, even for MnS_2 , isothermal heat absorption must be small since the enthalpy increment over a 0.04°K interval at the maximum is only 3.5 cal/mole. The large naturally occurring single crystals employed may have contributed to the relative sharpness of the transition in comparison with those in other antiferromagnetic substances studied in the form of fine crystalline particles of synthesized samples. X-ray diffraction studies of MnS_2 in a cryostat on a horizontal Ge goniometer showed the same profiles of the split α_1 and α_2 lines above and below the transition. The structure seemingly remained cubic, with $a=6.096$ Å at 4°K .

For MnTe_2 the structure also remains cubic with no indication of deformation on cooling through the transition region. The lattice constant at 4°K is $a=6.931$ Å.

Analysis of the available magnetic susceptibility data by Lin¹⁸ and by Hastings *et al.*⁵ on MnTe_2 gives level splittings rather similar to those obtained for MnS_2 . The reciprocal susceptibility calculated for $E_1/k=180^\circ\text{K}$ and $E_2/k=800^\circ\text{K}$ is shown as a function of temperature in Fig. 3 together with the experimental data.

The results indicate, just as for MnS_2 , that the higher levels are only partially populated at 298°K . Although the temperature region of the Schottky anomaly is indicated to go below that of the λ -type transition in Fig. 4, resolution of the two phenomena is probably not feasible in this region. As evidenced by the broadness of the heat capacity maximum, the degree of cooperation is smaller than for MnS_2 where the Schottky contribution is less because of higher population of the ground state. Other effects might, however, be as—or more—important.

An estimate of the MnTe_2 lattice heat capacity was obtained in the same way as for MnS_2 by calculating Debye θ 's outside the transition region after subtracting the assumed Schottky contribution from the observed heat capacity above the λ transition (see Fig. 4). The resulting transitional contribution to the entropy at 298°K is then $\Delta St=2.4$ cal/mole $\cdot^\circ\text{K}$. The entropy not yet acquired in the Schottky transition is 0.60 cal/mole $\cdot^\circ\text{K}$. Thus, about 85% of the expected contribution is accounted for. Evaluation of the lattice heat capacity by other more accurate methods (e.g., inelastic neutron scattering) is a desideratum.

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