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

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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 MnS_2 and at 83.0°K for $MnTe_2$. Entropies, enthalpies, and Gibbs energy function values are calculated and tabulated. At 298.15°K they are: $S°=23.88$ cal/mole·°K, $H°-H_0°=3384$ cal/mole, $-[(G°-H_0°)/T]=12.258$ cal/mole·°K for MnS_2 and 34.66, 4416, and 19.847 for $MnTe_2$. The clearly cooperative entropy increments are only 0.71 cal/mole·°K for MnS_2 and 0.80 for $MnTe_2$. 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 MnS_2 and $MnTe_2$, 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 chloridelike 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 $Mn_2P_2O_7$, 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. Worthring 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 $a=6.102\pm0.001$ Å, which agrees well with earlier values[9] (6.109±0.005 Å*,[10] 6.107±0.003 Å,[11] 6.1008±0.0001 Å at 29°C,[12] and 6.1016 A 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 $a = 6.954 \pm 0.001$ Å, in good agreement with three earlier results (6.957 ± 0.002 Å,[2] 6.951 ± 0.002 Å,[14] and 6.958 Å [15]).

Cyrogenic Technique

The heat capacities were measured in the Mark II cryostat[16] 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, voltage, and time are based upon calibrations or standardizations performed by the U.S. National Bureau of Standards.

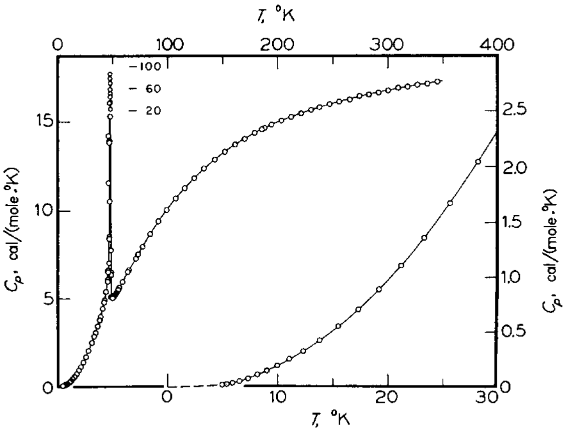

FIG. 1. Heat capacity of MnS_2 (hauerite).

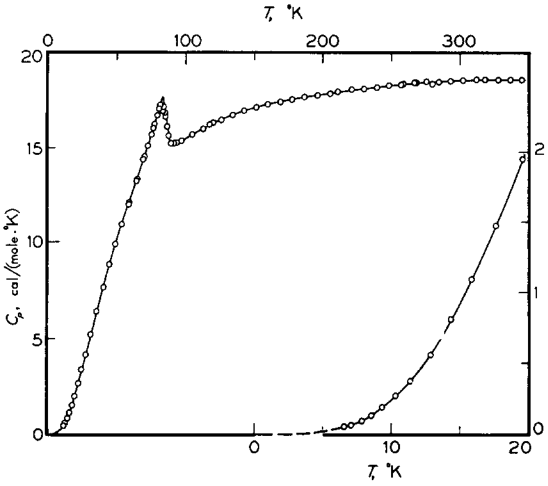

FIG. 2. Heat capacity of $MnTe_2$.

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 cal/mole·°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 cal/mole·°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 program[17] 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 ±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]

Maganese disulfide MnS_2 (hauerite); 1 mole = 119.07 g

T	C_p
Series I	
64.99	6.653
71.05	7.318
77.40	8.001
84.23	8.725
91.59	9.419
99.39	10.074
107.43	10.707
115.56	11.291
124.11	11.858
133.33	12.409
142.76	12.911
151.99	13.350
161.13	13.741
170.15	14.076
179.18	14.399
188.20	14.683
Series II	
4.98	0.020
5.38	0.024
5.88	0.035
6.54	0.051
7.31	0.076
8.15	0.111
9.04	0.154
9.99	0.205
11.05	0.255
12.32	0.324
13.82	0.427
15.53	0.555
17.34	0.709
19.21	0.891
21.20	1.107
23.32	1.364
25.63	1.673
28.20	2.043
31.08	2.496
34.38	3.066
38.13	3.792
42.43	4.829
ΔHt Run A	
51.26	5.176
56.34	5.657
Series III	
33.13	2.850
36.32	3.432
39.09	3.993
41.02	4.435
42.77	4.905
44.36	5.419
ΔHt Run B	
50.12	5.031
Series IV	
ΔHt Run C	
Series V	
45.71	6.024
46.62	6.612
47.01	7.055
47.36	8.474
47.63	14.114
47.77	34.74
47.84	78.14
47.90	87.00
47.94	68.93
48.00	37.32
48.13	15.36
48.51	6.511
Series VI	
46.57	6.586
47.43	10.537
47.81	58.08
47.89	86.88
47.93	87.26
47.97	45.65
48.06	23.73
48.41	7.771
Series VII	
ΔHt Run D	
49.05	5.081
49.58	4.992
50.11	5.045
50.63	5.059
51.40	5.127
52.41	5.248
53.40	5.324
55.28	5.533
59.23	5.985
64.43	6.590
73.39	7.574
ΔH Run E	
ΔH Run F	
185.71	14.603
194.63	14.862
203.52	15.09
212.49	15.31
221.55	15.51
230.59	15.70
238.09	15.85
247.24	16.02
256.32	16.17
265.30	16.29
274.17	16.48
282.99	16.54
291.75	16.67
300.49	16.77
309.27	16.92
318.11	17.00
327.03	17.08
336.11	17.15
345.33	17.26

Manganese ditelluride, $MnTe_2$; 1 mole = 310.16 g

T	C_p
Series I	
257.01	18.39
268.21	18.48
278.97	18.47
Series II	
117.57	16.27
125.37	16.51
134.12	16.78
142.68	16.99
151.16	17.19
159.79	17.33
168.73	17.50
177.79	17.61
186.86	17.74
196.02	17.84
205.17	17.93
Series III	
6.58	0.041
7.05	0.059
7.85	0.088
8.52	0.124
9.31	0.182
10.29	0.265
11.40	0.370
12.85	0.558
14.36	0.805
15.88	1.093
17.63	1.472
19.60	1.949
22.12	2.612
24.79	3.343
27.53	4.124
31.18	5.155
35.62	6.416
40.25	7.666
44.90	8.854
49.28	9.930
53.66	10.955
58.59	12.076
64.07	13.296
70.03	14.587
76.46	16.08
83.46	16.98
91.55	15.29
Series IV	
58.75	12.114
64.36	13.370
69.11	14.391
72.60	15.16
75.19	15.77
77.33	16.29
79.23	16.77
80.75	17.16
81.74	17.34
82.40	17.44
83.00	17.52
83.60	17.41
84.25	17.22
84.92	16.96
85.59	16.66
86.28	16.11
87.33	15.67
89.47	15.23
93.92	15.27
Series V	
ΔH Run A	
96.88	15.40
104.66	15.73
112.46	16.05
120.05	16.34
ΔH Run B	
211.17	18.00
220.88	18.12
230.00	18.17
239.19	18.25
248.46	18.33
257.67	18.40
266.84	18.46
275.94	18.53
285.02	18.55
294.05	18.58
303.12	18.62
312.27	18.65
Series VI	
318.84	18.64
328.12	18.64
337.37	18.67
345.80	18.67

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[a] Units: calorie, mole, degree Kelvin.

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

Manganese disulfide, MnS_2 (hauerite); 1 mole = 119.07 g

T	C_p	$S°$	$H°-H_0°$	$-(G°-H_0°)/T$
5	0.018	0.006	0.02	0.002
10	0.196	0.063	0.48	0.015
15	0.513	0.198	2.20	0.051
20	0.975	0.405	5.85	0.112
25	1.584	0.685	12.19	0.198
30	2.322	1.037	21.90	0.307
35	3.182	1.458	35.61	0.441
40	4.195	1.947	53.97	0.598
60	6.079	4.572	183.5	1.514
70	7.212	5.595	250.0	2.024
80	8.276	6.629	327.5	2.535
90	9.251	7.661	415.2	3.047
100	10.129	8.682	512.2	3.560
110	10.912	9.684	617.5	4.071
120	11.607	10.664	730.1	4.580
130	12.222	11.618	849.4	5.085
140	12.767	12.544	974.4	5.585
150	13.251	13.442	1104.5	6.079
160	13.684	14.311	1239.2	6.566
170	14.070	15.153	1378.0	7.047
180	14.418	15.967	1520.5	7.520
190	14.730	16.755	1666.2	7.985
200	15.01	17.518	1815.0	8.443
210	15.26	18.256	1966.4	8.893
220	15.49	18.972	2120.2	9.335
230	15.70	19.665	2276.1	9.769
240	15.89	20.337	2434.0	10.195
250	16.06	20.989	2593.8	10.614
260	16.22	21.622	2755.2	11.025
270	16.37	22.237	2918.1	11.429
280	16.51	22.835	3082.5	11.826
290	16.65	23.416	3248.3	12.216
300	16.77	23.983	3415.4	12.598
310	16.89	24.535	3583.7	12.975
320	17.01	25.073	3753.2	13.344
330	17.11	25.598	3923.8	13.708
340	17.20	26.110	4095.4	14.065
350	17.28	26.610	4267.8	14.416
273.15	16.41	22.43	2970	11.555
298.15	16.75	23.88	3384	12.528

Manganese ditelluride, $MnTe_2$; 1 mole = 310.16 g

T	C_p	$S°$	$H°-H_0°$	$-(G°-H_0°)/T$
5	0.019	0.006	0.023	0.002
10	0.228	0.060	0.471	0.013
15	0.918	0.266	3.126	0.058
20	2.041	0.676	10.382	0.157
25	3.403	1.275	23.94	0.318
30	4.829	2.022	44.52	0.538
35	6.233	2.872	72.19	0.810
40	7.600	3.794	106.79	1.125
45	8.879	4.765	148.05	1.475
50	10.099	5.764	195.5	1.854
60	12.391	7.810	308.1	2.675
70	14.588	9.886	443.0	3.557
80	16.97	11.984	600.5	4.476
90	15.21	14.053	766.2	5.540
100	15.54	15.667	919.4	6.473
110	15.96	17.169	1077.0	7.378
120	16.33	18.574	1238.5	8.253
130	16.65	19.893	1403.4	9.098
140	16.92	21.138	1571.3	9.914
150	17.16	22.313	1741.8	10.702
160	17.35	23.427	1914.3	11.462
170	17.52	24.484	2088.7	12.198
180	17.66	25.489	2264.6	12.908
190	17.78	26.448	2441.8	13.596
200	17.89	27.362	2620.1	14.262
210	17.99	28.238	2799.5	14.906
220	18.08	29.08	2979.9	15.53
230	18.17	29.88	3161.1	16.14
240	18.25	30.66	3343.2	16.73
250	18.33	31.40	3526.1	17.30
260	18.41	32.12	3709.8	17.86
270	18.47	32.82	3894.2	18.40
280	18.53	33.49	4079.2	18.92
290	18.58	34.14	4264.8	19.44
300	18.62	34.77	4450.8	19.94
310	18.64	35.39	4637.1	20.43
320	18.65	35.98	4823.5	20.90
330	18.65	36.55	5010.0	21.37
340	18.66	37.11	5196.6	21.82
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 $\Delta St=0.71$ cal/mole·°K and $\Delta Ht=33$ cal/mole for MnS_2 (see Table III). For $MnTe_2$ a similar procedure over the range 54–93°K leads to $\Delta St=0.55$ cal/mole·°K and $\Delta Ht=41$ 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

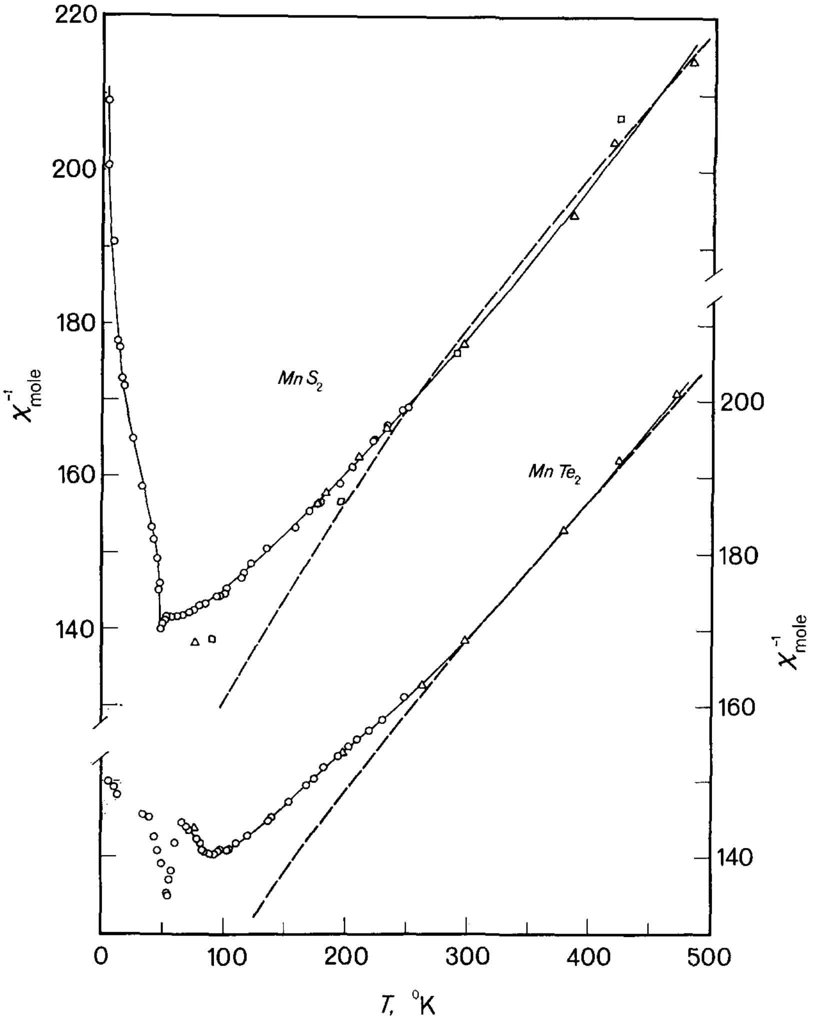

FIG. 3. Reciporcal molar susceptibilities of NnS_2 and $MnTe_2$ (corrected for diamagnetism) vs temperature. △ represents data by Haraldsen and Klemm[4]; □ represents data by Hastings *et al.*[5]; ○ represents data by Lin[18]; — represents experimental data; - - - represents calculated data assuming 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	$H_{T_2}-H_{T_1}$	$H_{55}-H_{44}$
		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			$H_{55}°-H_{44}°=81.8$ $H_{44}°-H_{25}°=60.6$ $H_{65}°-H_{55}°=60.8$		
			$H_{65}°-H_{25}°=203.2$		
Noncooperative contribution			$H_{65}°-H_{25}°=170.4$ $\Delta Ht=33$ $\Delta St=0.71$		
$T_t=47.93°K$					

[a] Units: calorie, 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

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

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 $E_1/k=190$°K and $E_2/k=900$°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.,

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

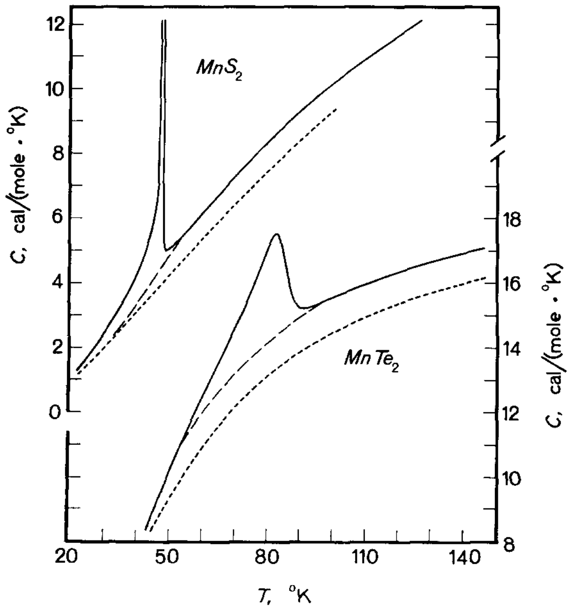

FIG. 4. Heat capacities of MnS_2 and $MnTe_2$ in the transition region. — represents experimental data; - - - represents estimated lattice heat capacity; -- represents lattice heat capacity plus Schottky contribution.

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 A in hauerite and 2.27 A 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 $298°\text{K}=2.6$ 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. Dimmock[20] has discussed these requirements for the magnetic transition in $MnSe_2$ and found that the low-temperature structure cannot transform continuously 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 $a=6.096$ A 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 Lin[18] 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 $E_1/k=180$°K and $E_2/k=800$°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·°K. The entropy not yet acquired in the Schottky transition is 0.60 cal/mole·°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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