Low Temperature Research. XLIII. Atomic Heat of alpha-manganese and gamma-manganese between 10° and 273°K [1]

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The atomic heats of alpha- and gamma-manganese have been measured between ~10 and 273 °K. From the experimental data the following values have been calculated: for the entropies (at 25 °C), $7{,}6_5$ and $7{,}9_8$ Clausius; for the coefficients γ of the electronic heat ($C_e = \gamma T$), $32{,}_8 \cdot 10^{-4}$ and $24{,}_8 \cdot 10^{-4}$ cal/deg²·g-atom, respectively. The γ values are valid below 20 °K and the corresponding characteristic temperatures, Θ^*, are 415° and 373°.

A systematic study of the atomic heat of the transition elements has been carried on for years by Clusius and coworkers; in the present paper the results about manganese, in the two phases alpha and gamma, are reported.

As to alpha-manganese, atomic heat measurements have already been carried out at low temperatures by Guthrie et al. (1,8 – 4,2 °K)[2], by Wolcott (1,2 – 20 °K)[3], by Booth et al. (11 – 20 °K)[4], by Armstrong et al. (14 – 22 °K)[5], and by Elson et al. (16 – 22 °K)[6]. These authors, however, found differing values for the electronic heat coefficient, γ, ranging from $28 \cdot 10^{-4}$ to $43 \cdot 10^{-4}$ cal/deg²·g-atom (see Table 6).

Kelley (53 – 298 °K)[7] and Shomate (54 – 301 °K)[8] measured alpha-manganese at intermediate temperatures. The former found that the plot C_p vs. T "... is regular throughout the temperature range studied ...", while the latter pointed out "... a small 'hump' ... extending over the temperature range 63 – 103 °K, with the peak of the 'hump' occurring about 95 °K...", and further "... Kelley did not report a 'hump' in his specific heat curve of alpha-manganese. However, recalculation of his original data showed his specific heat value at 88,2 °K to be in error. The corrected value is 3,251 cal/g-atom or about 4 percent higher than the value 3,130 cal/g-atom which he reported. Thus, re-examination of his specific heat curve indicated a 'hump' of magnitude comparable to that in the present measurements ..."

The above, together with the lack of data in the range between ~20 and ~50 °K made a revision of the atomic heat of alpha-manganese desirable. On the other hand, extending the measurements on gamma-manganese down to liquid and solid hydrogen temperatures was of interest, as the only data available were those of Shomate (52 – 298 °K)[8].

Experimental

According to our usual procedure, the samples, in the shape of cylinders, were used directly as calorimeters, after having glued on each of them a constantan wire (⌀ 0,05 mm) for heating and a lead wire (⌀ 0,08 mm) as resistance thermometer. Both Pb-thermometers were checked by measuring their resistance at melting ice temperature (273.16 °K) and by comparing them with O_2 and H_2 vapour pressure thermometers.

Alpha-manganese had been obtained electrolytically at a high degree of purity. Mn percentage was 99.95. The analysis gave the following percentages of impuri-

[1] XLII. Die Atom- und Elektronenwärme sowie die Entropie des Rheniums zwischen 10 und 298,2 °K — Z. Naturforschg. **19 a**, 1075 [1964].

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ties: Fe (0.01), Cu (0.01), C (0.01), O_2 (between 0.01 and 0.001), Si (0.001), Ni (0.001), H (2 cc per 100 g). Material of the same purity was employed to prepare the gamma-manganese sample. Gamma-manganese was stabilized by adding $\sim$ 6 percent by weight of copper (the experimental heat capacities of this sample have been corrected for the Cu contents by using the atomic heat data for copper given by KOK et al. [9] and by GIAUQUE et al. [10]). It was proved roentgenographically that in both samples only negligible amounts of not desired phases were present.

Data concerning the samples are listed in Tab. 1.

	alpha-manganese	gamma-manganese
Dimensions of the cylinder (height · diameter), mm	50 · 20	50 · 20
Weight of the cylinder, g	111, 4472	110, 3660 103, 8544 g Mn +6,5116 g Cu
Resistance of the constantan wire at 0°C, Ohm	393	387
Resistance of the lead wire at 0°C, Ohm	481	951
Atomic weight M	54,94	54,94
Density ϱ at 20 °C, g/cm³	7,44 (cf. [11])	7,2 (cf. [12])
Linear expansion coefficient α at 20 °C, deg^{-1}	$22{,}8 \cdot 10^{-6}$ (cf. [13])	$14{,}75 \cdot 10^{-6}$ (cf. [14])
Compressibility β at 20 °C (extrapolated value), cm²/kg	$7{,}872 \cdot 10^{-7}$ (cf. [15])	$7{,}872 \cdot 10^{-7}$ (cf. [15])
C_p at 20 °C (extrapolated from our measurements), cal/deg. g-atom	6,232	6,651
$(C_p - C_v)$ at 20 °C (calculated)	$0{,}301_4$	$0{,}130_4$
$A = (C_p - C_v)/C_p^2 \cdot T$	$2{,}647 \cdot 10^{-5}$	$1{,}005 \cdot 10^{-5}$

Table 1. Data concerning the alpha- and gamma-manganese samples, together with the values used for converting C_p into C_v by the formula: $(C_p - C_v) \approx (3\,\alpha)^2\, M\, T/\varrho\, \beta = A\, C_p^2\, T$.

Results and Discussion

1. For alpha-manganese the experimental values of C_p are listed in Table 2 and plotted vs. temperature in Fig. 1. In Table 4 the C_p values from the smoothed curve are given together with the corresponding C_v and $\Theta = f(C_v)$, calculated in the usual way by using the quantities specified in Table 1. In Fig. 3 the DEBYE Θ are plotted vs. T.

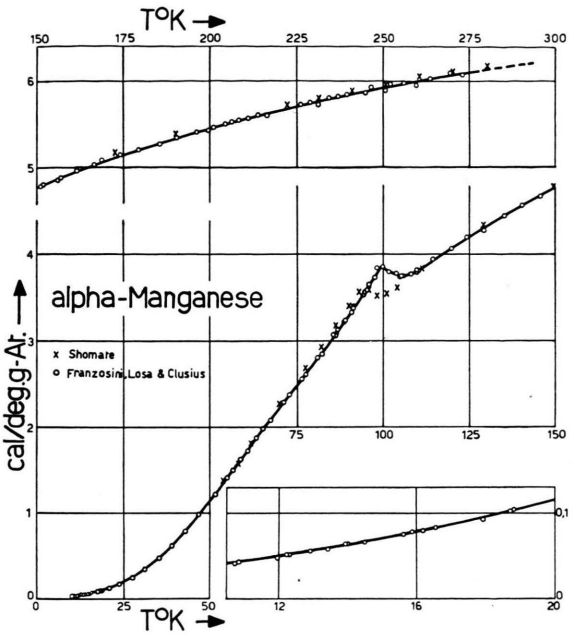

Fig. 1. Atomic heat C_p vs. temperature for alpha-manganese between 10 and 273 °K; in the lower right hand corner the region between $\sim$ 10 and 20 °K is magnified. Circles: this paper; crosses: SHOMATE.

Our results confirm the existence of the anomaly in the curve C_p vs. T already found by SHOMATE [8]. However, our data show that the 'peak' appears at about 100 °K, instead of 95 °K, as stated by SHOMATE in his paper.

On the other hand, SHULL et al. (1953) [16], by neutron diffraction measurements, revealed that alpha-manganese is antiferromagnetic, showing a NÉEL temperature just at 100 °K, which very satisfactorily agrees with our present calorimetric results.

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Series	T, °K	C_p	Series	T, °K	C_p
I/10	10,74	0,0415	V/9	97,92	3,744
I/1	10,87	0,0439	IV/14	98,06	3,859
I/6	11,95	0,0488	IV/15	99,99	3,865
I/2	12,22	0,0523	IV/16	101,96	3,807
I/11	12,28	0,0530	IV/17	104,01	3,784
I/15	12,92	0,0567	II/10	104,84	3,732
I/7	13,40	0,0589	IV/7	105,46	3,758
I/3	13,94	0,0652	IV/18	106,09	3,773
I/12	13,98	0,0650	IV/19	108,25	3,783
I/16	14,50	0,0668	II/11	109,99	3,831
I/8	15,62	0,0763	IV/8	110,09	3,809
I/13	15,86	0,0788	IV/20	110,40	3,828
I/4	16,20	0,0804	II/12	114,67	3,947
I/17	16,53	0,0839	II/13	119,96	4,079
I/9	17,92	0,0934	II/14	124,58	4,207
I/14	18,70	0,1026	II/15	129,60	4,287
I/5	18,81	0,1052	II/16	135,33	4,461
I/18	18,94	0,1060	II/17	140,25	4,579
I/19	21,13	0,1303	II/18	145,77	4,683
I/20	24,02	0,1775	V/1	151,14	4,786
I/21	27,84	0,2587	II/19	152,03	4,812
I/22	31,27	0,3481	V/2	156,18	4,861
I/23	35,29	0,4812	II/20	157,23	4,884
I/24	39,20	0,6307	V/3	161,74	4,970
I/25	42,99	0,7963	II/21	162,38	5,000
I/26	46,90	0,9856	V/4	166,73	5,039
I/27	51,58	1,225	II/22	168,84	5,097
I/28	55,14	1,420	II/23	174,18	5,157
II/1	56,95	1,504	II/24	179,30	5,208
I/29	58,96	1,628	II/25	185,25	5,275
II/2	61,03	1,725	II/26	190,33	5,355
I/30	63,54	1,884	II/27	196,16	5,417
II/3	65,69	1,986	III/1	199,55	5,442
I/31	67,62	2,092	II/28	201,22	5,470
II/4	71,43	2,301	III/2	204,73	5,514
IV/1	72,99	2,390	II/29	206,48	5,539
II/5	76,37	2,570	III/12	208,52	5,561
IV/2	77,55	2,624	III/3	211,21	5,583
II/6	81,02	2,820	III/13	213,97	5,609
IV/3	81,88	2,860	III/4	216,61	5,612
IV/9	85,50	3,077	III/14	226,18	5,739
II/7	86,18	3,070	III/5	228,97	5,764
IV/4	87,00	3,135	III/15	231,34	5,739
IV/10	87,03	3,084	III/6	234,41	5,817
IV/11	88,52	3,224	III/16	237,20	5,842
V/5	89,10	3,247	III/7	239,62	5,848
II/8	90,75	3,341	III/17	244,95	5,880
IV/5	91,35	3,392	III/8	246,58	5,946
IV/12	91,69	3,408	III/18	250,76	5,902
V/6	94,69	3,544	III/9	252,37	5,981
V/8	94,93	3,579	III/19	256,15	5,992
IV/6	95,58	3,604	III/10	259,81	5,959
II/9	96,02	3,626	III/20	263,67	6,044
IV/13	96,20	3,667	III/21	269,58	6,109
V/7	97,82	3,746	III/11	273,00	6,080

Table 2. The measured atomic heats, C_p, of alpha-manganese in cal/deg·g-atom.

Recently a number of investigators have been deeply interested in the magnetic properties of alpha-manganese. In particular, TAUER et al. [17] in analysing the atomic heat and the antiferromagnetic structure of this metal (their analysis was grounded on the above mentioned data by SHOMATE as well as on the paper by KASPER et al. [18]) pointed out that at low temperatures ($T<25$ °K) the atomic heat at constant pressure of alpha-manganese may be expressed as a sum of three terms as follows:

$$C_p(\text{total}) = \frac{464{,}5}{\Theta^{*3}} T^3 + B T^3 + \gamma T\,, \qquad (1)$$

B being the spin wave coefficient.

If eq. (1) is valid, it is still possible to evaluate the electronic heat coefficient, γ, through a linear extrapolation in a plot $(C_p \sim C_v)/T$ vs. T^2, which we have done (see Fig. 2), obtaining $\gamma = 32{,}_8 \cdot 10^{-4}$ cal/deg²·g-atom, but, unless B is known, it is not possible to calculate Θ^*. Nevertheless, arbitrarily assuming B to be negligible in comparison with

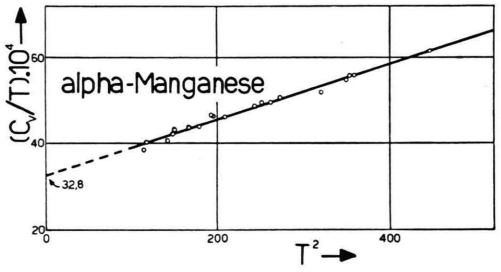

Fig. 2. C_v/T vs. T^2 for the evaluation of the electronic heat coefficient γ of alpha-manganese. Extrapolated value: $\gamma = 32{,}_8 \cdot 10^{-4}$ cal/deg²·g-atom.

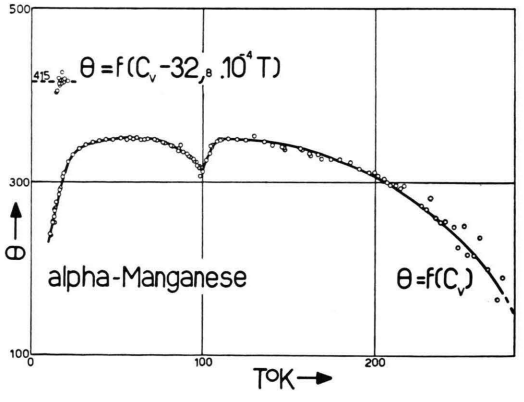

Fig. 3. The continuous curve shows the characteristic DEBYE temperatur $\Theta = f(C_v)$ for alpha-manganese when the observed C_v values are used in the calculation. We also report (for $10° < T < 21$ °K) the values of Θ^*, which may be calculated after deducting the quantities $C_e = 32{,}_8 \cdot 10^{-4} \cdot T$ from the above C_v values.

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$464{,}5/\Theta^{*3}$, we made an evaluation of Θ^*, in order to obtain a figure comparable with those of other authors and deduced in a similar way. The Θ^* value so calculated is 415° (see Table 6).

In Table 6 the γ values obtained by different authors are listed: our figure ($32{,}_8 \cdot 10^{-4}$) is in full agreement with that of GUTHRIE et al., measured at liquid helium temperatures. Alpha-manganese has an abnormally high electronic heat, as often is the case for transition metals.

2. The experimental values of C_p for gamma-manganese (cal/deg·g-atom) are tabulated in Table 3 and graphically shown in Fig. 4, while the interpolated C_p are reported in Table 5, together with the corresponding C_v and $\Theta = f(C_v)$ values.

Series	T, °K	C_p	Series	T, °K	C_p
I/5	12,90	0,0526	II/11	112,22	4,069
I/13	13,20	0,0534	II/12	121,43	4,349
I/1	13,25	0,0535	II/13	126,14	4,437
I/9	13,46	0,0565	II/14	130,74	4,565
I/6	14,44	0,0609	II/15	135,94	4,684
I/10	14,51	0,0630	II/16	140,76	4,773
I/2	14,55	0,0625	II/17	145,48	4,913
I/14	14,67	0,0637	II/18	150,76	4,996
I/11	16,18	0,0777	II/19	155,61	5,090
I/3	16,32	0,0794	II/20	160,39	5,180
I/7	16,73	0,0831	II/21	165,60	5,254
I/15	16,78	0,0831	II/22	170,42	5,368
I/12	18,39	0,1017	II/23	181,84	5,499
I/4	18,47	0,1022	II/24	186,87	5,580
I/8	19,11	0,1092	II/25	191,84	5,669
I/16	19,46	0,1141	II/26	198,81	5,741
I/19	21,95	0,1505	IV/1	198,98	5,744
I/17	22,06	0,1491	II/27	204,18	5,806
I/20	24,80	0,2074	II/28	209,44	5,886
I/18	25,04	0,2125	IV/2	210,32	5,887
I/21	28,13	0,2946	II/29	214,48	5,949
I/22	31,97	0,4133	IV/3	215,77	5,931
I/23	36,35	0,5799	IV/13	218,97	5,963
I/24	41,01	0,7854	IV/4	223,05	6,016
I/25	45,17	0,9872	IV/14	224,66	6,048
I/26	49,55	1,212	IV/5	228,79	6,095
I/27	58,67	1,693	IV/15	230,14	6,076
II/1	61,71	1,810	IV/6	234,47	6,135
I/28	66,48	2,118	IV/16	238,01	6,189
II/2	66,77	2,122	IV/7	239,94	6,209
II/3	71,34	2,354	IV/17	243,95	6,260
II/4	75,67	2,571	IV/8	247,75	6,272
II/5	79,86	2,782	IV/18	249,60	6,303
II/6	84,72	3,003	IV/9	253,66	6,327
II/7	89,13	3,175	IV/19	255,00	6,371
II/8	93,51	3,364	IV/10	259,29	6,381
III/1	93,83	3,363	IV/20	262,73	6,414
III/2	98,37	3,568	IV/11	267,38	6,456
III/3	102,90	3,707	IV/21	268,63	6,468
II/9	103,11	3,729	IV/12	273,38	6,518
II/10	107,69	3,901			

Table 3. The measured atomic heats, C_p, of gamma-manganese in cal/deg·g-atom.

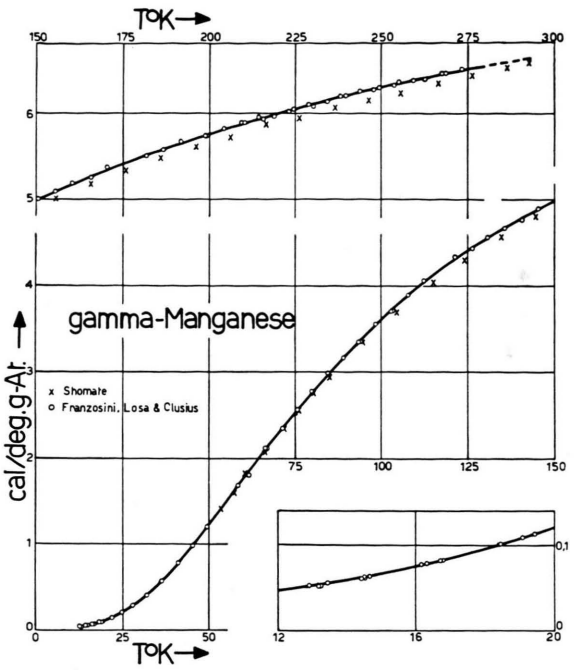

Fig. 4. Atomic heat C_p vs. temperature for gamma-manganese between 12 and 273 °K; in the lower right hand corner the region between 12 and 20 °K is magnified. Circles: this paper; crosses: SHOMATE.

Contrary to what happens in the case of alpha-manganese, the C_p vs. T curve for gamma-manganese shows no irregularities in the temperature range studied.

Availing ourselves of the measurements between 12 and 22 °K, we have drawn the diagram of Fig. 5 and, by extrapolating, have calculated a γ value of $24{,}_8 \cdot 10^{-4}$ cal/deg²·g-atom. Proceeding in a similar way as for alpha-manganese, from the slope of the curve C_v/T vs. T^2 a value $\Theta^* = 373°$ can be deduced.

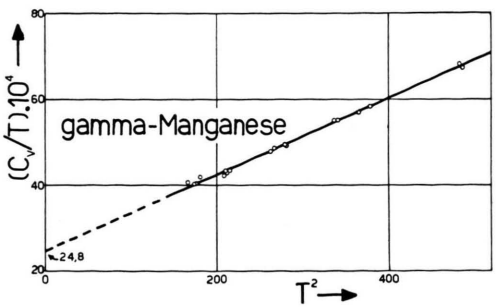

Fig. 5. C_v/T vs. T^2 for the evaluation of the electronic heat coefficient γ of gamma-manganese. Extrapolated value: $\gamma = 24{,}_8 \cdot 10^{-4}$ cal/deg²·g-atom.

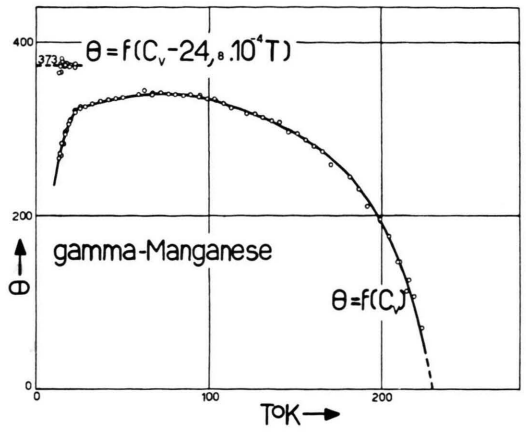

Fig. 6. The continuous curve shows the characteristic DEBYE temperature $\Theta=f(C_v)$ for gamma-manganese when the observed C_v values are used in the calculation. We also report (for $12°<T<22$ °K) the values of Θ^*, which may be calculated after deducting the quantities $C_e=24{,}8\cdot10^{-4}\cdot T$ from the above C_v values.

T, °K	C_p	C_p-C_v	C_v	$\Theta(C_v)$
10	0,038	—	0,038	230
15	0,072	—	0,072	280
20	0,117	—	0,117	317
25	0,194	—	0,194	334
30	0,314	—	0,314	341
35	0,469	—	0,469	345
40	0,664	—	0,664	348
45	0,888	0,001	0,887	350
50	1,133	0,002	1,131	351
60	1,681	0,004	1,677	349
70	2,226	0,009	2,217	348
80	2,761	0,016	2,745	343
90	3,308	0,026	3,282	332
100	3,869	0,040	3,829	312
110	3,816	0,042	3,774	349
120	4,083	0,053	4,030	350
130	4,332	0,065	4,267	348
140	4,570	0,077	4,493	343
150	4,778	0,091	4,687	338
160	4,950	0,104	4,846	333
170	5,094	0,117	4,977	329
180	5,222	0,130	5,092	324
190	5,345	0,144	5,201	318
200	5,464	0,158	5,306	308
210	5,574	0,173	5,401	297
220	5,677	0,188	5,489	284
230	5,775	0,203	5,572	267
240	5,875	0,219	5,656	245
250	5,938	0,233	5,705	233
260	6,014	0,249	5,765	211
273,2	6,104	0,269	5,835	175

Table 4. Smoothed values of C_p, (C_p-C_v) and C_v in cal/deg ·g-atom, and of $\Theta=f(C_v)$ for alpha-manganese.

In Fig. 6, Θ vs. T is shown: for gamma-manganese the characteristic temperature, above 100 °K, drops more sharply than in the case of alpha-manganese, so that the curve intersects the abscissa at $T\sim229$ °K *.

T, °K	C_p	C_p-C_v	C_v	$\Theta(C_v)$
10	0,036	—	0,036	235
15	0,067	—	0,067	286
20	0,122	—	0,122	312
25	0,212	—	0,212	324
30	0,346	—	0,346	330
35	0,527	—	0,527	331
40	0,742	—	0,742	333
45	0,978	—	0,978	336
50	1,233	0,001	1,232	338
60	1,756	0,002	1,754	341
70	2,283	0,004	2,279	342
80	2,779	0,006	2,773	341
90	3,232	0,009	3,223	338
100	3,627	0,013	3,614	334
110	3,981	0,018	3,963	328
120	4,293	0,022	4,271	321
130	4,552	0,027	4,525	314
140	4,779	0,032	4,747	306
150	4,982	0,037	4,945	296
160	5,164	0,043	5,121	283
170	5,325	0,048	5,277	268
180	5,477	0,054	5,423	249
190	5,623	0,060	5,563	224
200	5,758	0,067	5,691	192
210	5,880	0,073	5,807	150
220	5,993	0,079	5,914	83
230	6,101	0,086	6,015	—
240	6,203	0,093	6,110	—
250	6,304	0,100	6,204	—
260	6,400	0,107	6,293	—
273,2	6,513	0,116	6,397	—

Table 5. Smoothed values of C_p, (C_p-C_v) and C_v in cal/deg ·g-atom, and of $\Theta=f(C_v)$ for gamma-manganese.

* At low temperatures pure manganese in the gamma-phase easily undergoes transformations, and therefore we preferred to employ a sample stabilized by addition of a few percent of copper.

To consider the C_p values for Mn and Cu in this sample as merely additive (according to our procedure) obviously is an approximation, which is likely not important for what concerns the total atomic heat, but which might imply some uncertainty when attempting to evaluate the electronic heat coefficient γ.

In fact, according to the opinion of ZIMMERMAN and SATO [19] the γ value for pure gamma-manganese might be one third to two thirds smaller than that deduced from an alloy containing 5% Cu. However, while the present paper was already in press, we read a freshly published work by Ho et al. [20], who reported a γ value of 9.20 mJ/deg²·g-atom (corresponding to $\sim22\cdot10^{-4}$ cal/deg²·g-atom), evaluated from measurements on pure gamma-manganese at $T<4{,}2$ °K: this value is satisfactorily close to that proposed by us ($24{,}8\cdot10^{-4}$ cal/deg²·g-atom).

[19] J. E. ZIMMERMAN and H. SATO, J. Phys. Chem. Solids **21**, 71 [1961].

[20] J. C. Ho and N. E. PHILLIPS, Phys. Letters **10**, 34 [1964].

$\gamma \cdot 10^4$	Θ*	Temperature range, °K	Authors
32,9	—	1,8—4,2	GUTHRIE, FRIEDBERG, and GOLDMAN[2]
43	—	1,2—20	WOLCOTT[3]
28	392	11—20	BOOTH, HOARE, and MURPHY[4]
35—40	—	14—22	ARMSTRONG and GRAYSON-SMITH[5]
42,1	410	16—22	ELSON, GRAYSON-SMITH, and WILHELM[6]
32,8	415	10—21	this paper

Table 6. Values of the electronic heat coefficient, γ (cal/deg^2·g-atom), for alpha-manganese.

3. Entropies at 25 °C have been calculated graphically as: $7{,}6_5$ cal/deg·g-atom for alpha-manganese and $7{,}9_8$ cal/deg·g-atom for gamma-manganese.

KELLEY, on the basis of his own measurements between ~50 °K and room temperature, calculated an entropy value of $7{,}61 \pm 0{,}06$, while SHOMATE, using his own data in the same temperature range, gave $7{,}59 \pm 0{,}04$ cal/deg·g-atom. Both these values are consistent with the one we have found for α-Mn.

As to gamma-manganese, our figure may be compared only with the one (remarkably lower) of SHOMATE, who calculated $7{,}72 \pm 0{,}04$ cal/deg·g-atom.

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Polarisationsoptische Temperaturmessung und Filterung bei Rubin-Laser

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Die Temperatur im Inneren eines homogenen Laser-Rubins läßt sich auf Grund seiner Doppelbrechung auf optischem Wege ermitteln, indem man ihn zwischen zwei gekreuzte Polarisatoren bringt und die spektrale Lage der Polarisations-Interferenzstreifen bestimmt. Im Gebiet der R-Linien-Fluoreszenz verschieben sich die Interferenzstreifen zwischen 18 und 32 °C mit der Temperatur nach kürzeren Wellenlängen; es ist $\Delta\lambda/\Delta T = -0{,}83$ Å/grad. Bei der Anregung eines Rubins mit einer stabförmigen Xe-Blitzröhre in einem elliptischen Reflektor erhöht sich im vorliegenden Fall die Temperatur beim Schwellenwert um 1,1 °C. Bei Verwendung einer wendelförmigen Röhre wird der Kristall um 3,1 °C erwärmt. Während bei der stabförmigen Röhre die Temperatur nach der Anregung im Laufe von ca. 10 min monoton auf die Umgebungstemperatur absinkt, nimmt sie bei der Wendellampe infolge Wärmeleitung von der heißen Quarzwendel zunächst beträchtlich zu. Mit Hilfe eines aus einer Kristallplatte und zwei GLAN-THOMSON-Prismen bestehenden einfachen Polarisations-Interferenz-Filters läßt sich die Güte eines Laser-Resonators auch in sehr eng benachbarten Spektralbereichen beliebig variieren.

Bei der Anregung von Festkörper-Lasern wird im Kristall ein Teil der Pumpstrahlung in Wärme umgewandelt. Im Grundgitter werden Schwingungen angeregt, die nach kurzer Zeit im thermodynamischen Gleichgewicht sind und eine Temperaturerhöhung hervorrufen. Auch durch die fluoreszierenden Leuchtzentren wird auf Grund des Pumpmechanismus stets Energie an das Gitter übertragen. Beim Rubin gehen z. B. die durch Lichtabsorption in den $^4F_1$- und $^4F_2$-Banden angeregten Cr^{3+}-Ionen strahlungslos in die beiden ^2E-Zustände über, wobei die Differenz der Anregungsenergie vom Gitter aufgenommen wird. Die Kopplung der Leuchtzentren an das Gitter zeigt sich bekanntlich auch in der Überlagerung von Schwingungs- und Elektronenübergängen, die man in den Absorptions- und Fluoreszenzspektren des Rubins und anderer Chromphosphore beobachtet[1].

Die Temperaturerhöhung bei einem Laser-Kristall hat verschiedenartige Konsequenzen. Einmal wird die Linienbreite mit steigender Temperatur vergrößert und die Quantenausbeute verringert, wodurch die Schwellenenergie für erzwungene Emission

[1] E. FICK u. G. JOOS, Handbuch der Physik, Bd. **28**, Spektroskopie II, Springer-Verlag, Berlin 1957.