$$\phi_{1,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\alpha_1(r;\,\epsilon)b_1(k)B_1(\hat{k}) \times\left[(\hat{k}_x^2-\hat{k}_y^2)\varphi_{x^2-y^2}+\frac{1}{\sqrt{3}}(3\hat{k}_z^2-1)\varphi_{3z^2-r^2}\right], \quad \text{(A7)}$$

where

$$\int_0^{r_0} r^2dr|\alpha_n(r;\,\epsilon)|^2=1.$$

The functions $b_n(k)$ are left indeterminate. They have a maximum absolute value of 1 at the point H, since the Kubic harmonics involved are correct only at H. We take $B_n(\hat{k})$ to be the proper normalization factor (in configuration space) for the angular part of the wave function. For instance, we write

$$|B_5(\hat{k})|^2=[\hat{k}_x^2(3\hat{k}_x^2-1)^2+\hat{k}_y^2(3\hat{k}_y^2-1)^2+\hat{k}_z^2(3\hat{k}_z^2-1)^2]^{-1},$$

which is singular on Λ, so that the function (A3) is indeterminate on Λ (and this corresponds to the Λ_3 degeneracy). It is easy to see that the angular part of the functions (A2) to (A7) satisfy all compatible symmetry requirements of Table II, for all directions in k space.

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Specific Heat of Gadolinium, Terbium, Dysprosium, Holmium, and Thulium Metals between 3 and 25°K*

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The specific heat of gadolinium, terbium, dysprosium, holmium, and thulium metals has been measured between 3 and 25°K using a germanium resistance thermometer. Anomalies, apparently associated with magnetic transformations in the metals themselves, were found for terbium at 16°K and for holmium at 17.5°K. Low-temperature peaks, probably resulting from impurities, were observed for gadolinium, terbium, and dysprosium. By assuming that the sum of the lattice and electronic specific heats of all these metals is given by the total C_p of nonmagnetic lutetium and by calculating the nuclear contribution from previous work below 4°K, the magnetic specific heat C_M has been determined. For terbium and dysprosium an exponential temperature dependence, $C_M=36T^{3/2}\exp(-23.5/T)$ and $C_M=107T^{3/2}\exp(-31/T)$ (T in °K, C_M in mJ/mole °K), respectively, was found. The results are in accord with current theories that take into account the strong basal anisotropy in the magnetic structure of these metals. For gadolinium $C_M=0.19T^{2.7}$ above 13°K, but the functional form of C_M is much less certain than for terbium and dysprosium. For holmium $C_M=1.5T^{3.2}$ represents the magnetic specific heat quite well below 8°K. There is theoretical justification for a T^3 temperature dependence of C_M for both gadolinium and holmium. The magnetic specific heat of thulium between 4 and 20°K can be given by $C_M=8.3T^{2.3}$; no theoretical predictions are available for this metal. The observed behavior of C_M for most of these rare earths can be correlated with existing data on magnetization and electrical resistivity.

I. INTRODUCTION

The observed total specific heat C_p of the lanthanides is, in most cases, the sum of four distinct components: the lattice specific heat C_L, the electronic specific heat C_E, the magnetic specific heat C_M, and the nuclear specific heat C_N. The component C_M is caused by interactions between the localized $4f$ electronic spins, and C_N results from splitting of the nuclear hyperfine levels by interaction with the $4f$ electrons. The heat capacity of most rare-earth metals has been measured between 0.4 and 4°K.[1] Consequently, the nuclear specific heat, which is the dominant contribution below 1°K, has been accurately separated from the other components of C_p. Some information was also obtained about C_L and C_E.

Much less is known about the magnetic specific heat. The reason is, at least partly, that the temperature range from 4 to 15°K, which is important for studies of C_M, has been assiduously avoided by low-temperature physicists. To correct this unfortunate situation, and because a considerable amount of theoretical work has recently been done on C_M, a program for measuring the

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† On leave of absence from the Technical University of Helsinki, Otaniemi, Finland.

[1] O. V. Lounasmaa, Phys. Rev. 134, A1620 (1964) and other papers listed therein.

heat capacity of all rare-earth metals between 3 and 25°K was started. Results on europium and ytterbium and a short report on ytterbium, terbium, and dysprosium have already been published[2]; the present paper discusses the data on gadolinium, terbium, dysprosium, holmium, and thulium; measurements on lanthanum, praseodymium, neodymium, and samarium will be published in a later paper; the remaining rare earths have not yet been experimentally investigated by us. In all cases, except gadolinium, the same specimens have been used in the measurements between 0.4 and 4°K, and between 3 and 25°K.

The heavier lanthanides, from gadolinium to lutetium, with the exception of ytterbium, form a group within which the individual metals are, in many respects, very similar indeed. Their outer electronic configuration is $5s^2$, $5p^6$, $6s^2$, $5d^1$. Their crystal structure is hcp, with the $c{:}a$ ratio ranging from 1.570 to 1.590, and their density increases monotonically from 7.868 g/cm^3 for gadolinium to 9.849 g/cm^3 for lutetium. With the exception of thulium and lutetium, all these metals are indisputably ferromagnetic at low temperatures.

After very briefly discussing the experimental procedure in Sec. II, the results for each of the five metals are presented in tabular and graphical form and also compared with earlier specific heat data in Sec. III. In Sec. IV the method employed for separating the various contributions to C_p is explained and the theoretical picture concerning C_M is examined. Finally, in Sec. V the magnetic specific heat of each metal is analyzed in detail and the anomalies observed in their heat capacity are discussed.

II. EXPERIMENTAL

For a full description of the cryostat and measuring procedure we refer to three earlier papers[2–4]; only the most important experimental features will be repeated here. The sample was cooled from 300 to about 13°K with H_2 exchange gas, which was subsequently effectively removed by cryopumping. A mechanical heat switch was then employed for reaching the starting temperature of 3°K. In this way no exchange gas was absorbed onto the surface of the specimen. A germanium resistance thermometer of type CG-1, manufactured by Radiation Research Co., was used. This thermometer had been calibrated at 43 different points, spaced about evenly in log T, from 2 to 27°K. The calibration accuracy is about 1 m°K at 3°K, 3 m°K at 10 and 20°K, and 10 m°K at 25°K. The estimated precision of the C_p values is, at these same temperatures, 0.6%, 0.6%, 0.4%, and 2%, respectively.[2] The results have been corrected for curvature due to the finite temperature increments used when measuring the specific heat; this correction was never more than 0.2%. The size of the temperature increments may be computed from the separation of successive points in Tables II–VI.

III. RESULTS

1. Gadolinium

The vacuum-distilled gadolinium specimen was purchased from Research Chemicals. The sample weighed 236.87 g (=1.5063 moles), and results of its impurity analysis are given in Table I. In contrast to the other metals discussed in this paper, the gadolinium sample was not the same as used previously[5] in measurements between 0.4 and 4°K. Probably the most important difference is that the earlier sample contained 0.54% of oxygen, as compared with 0.20% in the present specimen.

TABLE I. The impurity content of specimens (in weight %).[a]

Impurity	Specimen Gd	Tb	Dy[b]	Ho	Tm[c]
Ta	0.02	···	0.026	···	0.12
H	0.013	0.02	0.03	0.005	0.0006
C	0.029	0.14	0.008	0.07	0.014
N	0.001	0.01	0.004	0.07	0.20
F	0.008	···	0.045	···	0.024
O	0.20	0.12	0.092	0.21	0.10

[a] Chemical and spectrographic analyses performed at the Argonne National Laboratory.

[b] From H. E. Flotow and D. W. Osborne, Ref. 11. Additional metallic impurities are: Al: 0.04; Ba: 0.01; Er: 0.03; Eu: 0.01; Fe: 0.05; K: 0.13; Pr: 0.03; Th: 0.02; Y: 0.09.

[c] Additional metallic impurities are: Al: 0.03; Fe: 0.01; K: 0.01; Mn: 0.01; Na: 0.02; Ti: 0.01.

Three final runs were made without warming the metal above 25°K in the meantime. The results are given in Table II and are also plotted into Fig. 1. The most prominent feature in the heat-capacity curve is the peak observed between 3 and 5°K.

At their low-temperature end the present measurements may be compared with a number of earlier data.[5–7] In general, the different results disagree, sometimes by more than a factor of 2, but there definitely appears to be a maximum between 3 and 4°K. It has been demonstrated by Crane[6] and by Donald, Crane, and Zimmermann[7] that these discrepancies are caused by the Gd_2O_3 impurity in the specimens. A zone-refined gadolinium sample investigated by these authors gave quite a low specific heat near 4°K, although a peak was still observed at 3.7°K. After graphically removing the effects of this anomaly and by assuming $C_E = 11.27T$

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[2] O. V. Lounasmaa, Phys. Rev. **143**, 399 (1966); *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yagub (Plenum Press, Inc., New York, 1965), p. 901.

[3] O. V. Lounasmaa and R. A. Guenther, Phys. Rev. **126**, 1357 (1962).

[4] O. V. Lounasmaa, Phys. Rev. **133**, A211 (1964).

[5] O. V. Lounasmaa, Phys. Rev. **129**, 2460 (1963).

[6] L. T. Crane, J. Chem. Phys. **36**, 10 (1962).

[7] D. K. Donald, L. T. Crane, and J. E. Zimmermann (private communication).

TABLE II. The specific heat of gadolinium metal (mJ/mole °K). Experimental results. (At. wt: 157.25 g/mole.)

T	C_p	T	C_p	T	C_p
Run 1		10.059	623.5	5.8224	203.88
3.0651	211.25	10.818	764.9	6.3981	233.49
3.3316	249.35	11.606	935.3	7.0127	273.15
3.6313	282.34	12.391	1126.7	7.6379	323.0
3.9749	193.47	13.213	1359.1	8.2759	385.6
4.4084	170.85	14.108	1646.7	8.9640	466.7
		15.124	2007.1	9.6887	569.5
Run 2		16.370	2510.4	10.443	693.2
3.2188	233.10	17.805	3158	11.224	846.5
3.5105	271.16	19.286	3904	12.010	1025.4
3.7948	232.17	20.772	4711	12.729	1221.2
4.1807	175.84	22.339	5617	13.345	1390.1
4.6131	170.72	24.037	6655	13.753	1518.1
5.0651	177.86			14.408	1742.8
5.5535	193.00	Run 3		15.583	2189.5
6.1205	218.38	3.7257	278.01	16.972	2776.6
6.7261	252.02	3.8685	207.48	18.467	3483
7.3317	295.07	4.0283	182.60	19.979	4267
7.9551	352.3	4.2037	173.93	21.529	5137
8.6070	421.1	4.4795	170.32	23.184	6126
9.3278	505.8	4.8827	173.99	24.927	7258
		5.3283	185.23		

mJ/mole °K (cf. Secs. IV.1 and IV.2) and $C_M = C_N = 0$, we obtain a Debye $\Theta = 195$°K for this gadolinium specimen.

Between 15 and 25°K the present results may be compared with those of Griffel, Skochdopole, and Spedding,[8] our values being consistently about 3% higher. The discrepancy is somewhat larger than the estimated experimental errors.

2. Terbium

The terbium specimen weighed 97.378 g (=0.61273 moles), slightly less than during the earlier experiments[9] between 0.4 and 4°K; this was a result of repolishing the sample. For results of chemical and spectrographic analyses we refer to Table I. The experimental data are given in Table III and Fig. 2. The sample was warmed to room temperature between runs 3 and 4. A rather small, previously unknown anomaly was detected at 4.5°K, and an irregularity in the heat capacity curve was found between 14 and 18°K. The latter anomaly shows hysteresis effects in that it did not fully develop unless the metal was first cooled well below 15°K. This

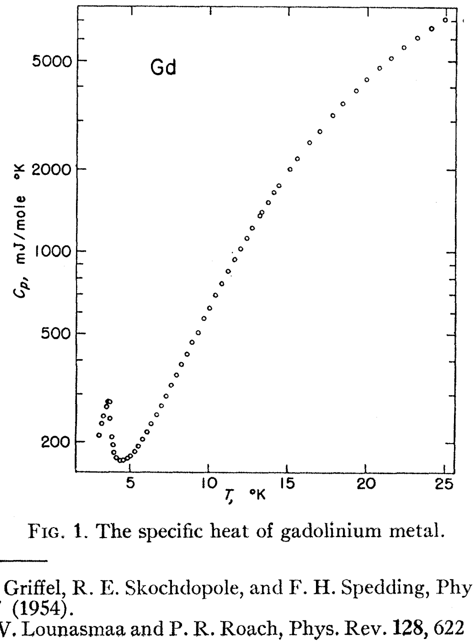

FIG. 1. The specific heat of gadolinium metal.

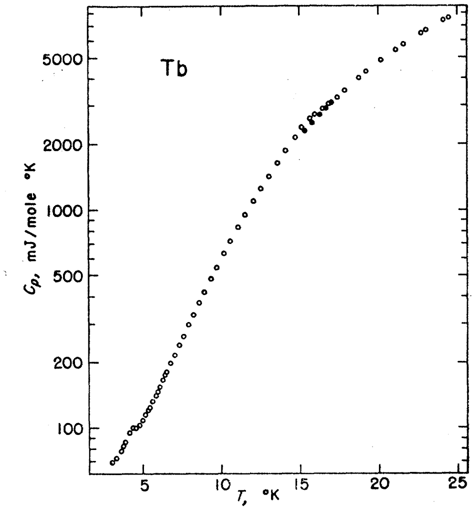

FIG. 2. The specific heat of terbium metal. Filled circles are points from run 5.

TABLE III. The specific heat of terbium metal (mJ/mole °K). Experimental results. (At. wt: 158.92 g/mole.)

T	C_p	T	C_p	T	C_p
Run 1		9.3867	630.0	12.583	1244.2
3.0866	69.54	10.222	630.0	13.628	1631.5
3.3466	72.77	11.134	829.4	14.738	2143.3
3.6302	78.10	12.093	1089.4	15.953	2719.8
3.9159	85.44	13.090	1423.1	17.388	3267
4.1877	94.20	14.147	1855.1	18.830	4013
4.5595	100.38	15.273	2415.7	20.197	4815
5.0001	108.11	16.568	2934.1	21.644	5713
5.4744	124.31	17.469	3282	23.085	6650
5.9570	145.95	19.290	4272	24.485	7629
6.4586	173.83	21.132	5386		
6.9862	209.46	22.746	6423	Run 4	
7.5534	256.31	24.120	7367	14.101	1829.0
8.1797	320.0			14.687	2111.0
8.8991	410.7	Run 3		15.197	2376.9
		4.4155	99.31	15.655	2600.7
Run 2		4.7959	103.00	16.080	2758.0
3.7918	92.30	5.2192	114.85	16.482	2888.5
4.1309	99.95	5.6541	131.75	16.934	3053
4.5102	106.28	6.0947	153.17	17.425	3262
4.9359	120.96	6.5537	179.94	17.917	3500
5.3876	140.24	7.0550	215.25		
5.8414	165.22	7.6195	263.18	Run 5	
6.3141	197.24	8.2472	328.1	15.378	2289.6
6.8099	239.48	8.9581	417.9	15.853	2509.0
7.3517	296.35	9.7571	543.6	16.286	2722.7
7.9574	374.6	10.635	716.0	16.688	2901.9
8.6300	482.1	11.584	944.6	17.064	3079

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[8] M. Griffel, R. E. Skochdopole, and F. H. Spedding, Phys. Rev. 93, 657 (1954).

[9] O. V. Lounasmaa and P. R. Roach, Phys. Rev. **128**, 622 (1962).

may be seen from Fig. 2, where the filled circles are experimental points from run 5; the specimen was cooled to only 15°K before this run was started.

As was discussed by Lounasmaa and Roach,[9] the specific heat of terbium has been measured below 4°K by many groups of investigators, whose results are not always in good accord. The present data overlap those of Lounasmaa and Roach[9] between 3 and 4°K, and the agreement between the two sets of results is better than 1%. This is reassuring in view of the fact that different thermometers and different calibration procedures were employed.

Between 15 and 25°K our data may be compared with the measurements of Jennings, Stanton, and Spedding.[10] At 15°K our results are about 15% higher than theirs, but the discrepancy, which is probably caused by the anomaly between 14 and 18°K, has almost disappeared by the time 25°K is reached. The data of Jennings *et al.*[10] show a slight bend in the C_p versus T curve between 15 and 16°K.

3. Dysprosium

The dysprosium specimen weighed 196.28 g (= 1.2079 moles), considerably less than during measurements between 0.4 and 4°K,[3] because of a hole drilled through the sample to make it fit into the calorimeter of Flotow and Osborne,[11] who also investigated the same piece of metal. The purity of the specimen is given in Table I and the experimental results are listed in Table IV and plotted into Fig. 3. Three runs were made without warming the metal above 25°K in the meantime. A distinct, previously unknown anomaly was observed around 5°K; between 7 and 25°K the heat capacity behaves regularly.

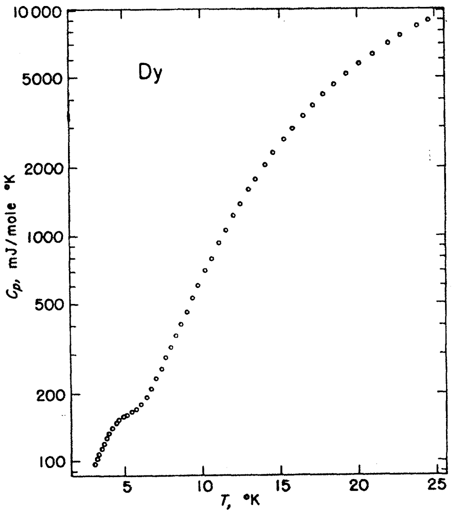

FIG. 3. The specific heat of dysprosium metal.

TABLE IV. The specific heat of dysprosium metal (mJ/mole °K). Experimental results. (At. wt: 162.50 g/mole.)

T	C_p	T	C_p	T	C_p
Run 1		19.346	5164	6.4357	192.60
4.4957	147.08	21.009	6334	7.0707	232.84
4.9774	157.66	22.773	7619	7.7051	288.23
5.5149	164.85	24.574	9021	8.3519	361.6
6.1081	178.19			9.0493	461.0
6.7398	209.20	Run 2		9.8274	601.2
7.3860	257.40	3.1237	96.97	10.675	794.7
8.0331	321.5	3.4003	107.25	11.577	1054.5
8.7071	407.7	3.7090	119.40	12.526	1379.2
9.4641	530.0	4.0455	132.56	13.481	1768.6
10.287	701.1			14.625	2313.8
11.160	927.5	Run 3		15.875	2978.1
12.094	1222.4	3.2691	102.16	17.164	3740
13.062	1591.9	3.5636	113.55	18.543	4634
14.109	2054.7	3.8880	126.46	20.133	5721
15.305	2667.5	4.2468	139.70	21.986	7049
16.571	3373	4.6802	152.08	23.849	8464
17.869	4183	5.1909	160.88		
		5.7696	169.22		

The specific heat of dysprosium has been measured previously by a number of investigators; the results below 4°K have been summarized by Lounasmaa and Guenther.[3] As in the case of terbium, large discrepancies, probably resulting from impurities, have been observed. The present sample exhibits two low-temperature anomalies, one around 2.3°K,[3] and another near 5°K. Other investigators have also found anomalies in their specimens below 4°K. One dysprosium sample studied by Dreyfus, Goodman, Trolliet, and Weil[12] was an exception in that the specific heat was regular and rather low and, with the assumption $C_M = 0$, gives a Debye Θ of 207°K at low temperatures. At the time the paper by Lounasmaa and Guenther[3] was written an analysis of this specimen was not available, but later Professor Dreyfus kindly sent a piece of his dysprosium metal to Argonne National Laboratory where it was subsequently analyzed. The most significant difference was the oxygen content, only 0.009% in the sample of Dreyfus *et al.* as compared with 0.092% in our specimen. This again shows how seriously an oxide impurity might affect the heat capacity, provided that the crystalline field splitting in the oxide is of the order of kT within the temperature range under investigation.

The internal consistency of the earlier[3] and the present data is better than 1% in the region between 3 and 4°K, where the measurements overlap.

In the temperature range above 4°K also, the heat capacity of dysprosium has been investigated by a number of people. Our data are in excellent agreement with the measurements of Flotow and Osborne[11] between 8 and 25°K, the two sets of values being almost indistinguishable. This is most reassuring since the measurements were carried out in different cryostats with different types of thermometers. Below 8°K the

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[10] L. D. Jennings, R. M. Stanton, and F. H. Spedding, J. Chem. Phys. **27**, 909 (1957).

[11] H. E. Flotow and D. W. Osborne, *Rare Earth Research II* (Gordon and Breach Publishers, Inc., New York, 1964), p. 233.

[12] B. Dreyfus, B. B. Goodman, G. Trolliet, and L. Weil, Compt. Rend. **253**, 1085 (1961).

platinum resistance thermometer of Flotow and Osborne was not sufficiently sensitive for observing the anomaly around 5°K, since too large temperature increments had to be used. Trolliet[13] has also measured the specific heat of dysprosium between 4 and 20°K. His data show more scatter than ours, but generally the discrepancy is less than 3%. Finally, the specific heat of dysprosium has been investigated between 15 and 300°K by Griffel, Shochdopole, and Spedding[14]; the agreement with our data is to within 1% in the overlapping region from 15 to 25°K.

In view of the good accord between the various measurements from 8 to 25°K it is evident that the observed specific heat truly represents dysprosium metal itself, the disturbing effects of the low temperature anomalies being mostly wiped out before 8°K is reached. This is, of course, very important for an analysis of C_p into its component parts.

4. Holmium

The holmium specimen weighed 85.540 g (=0.51864 moles), considerably more than the sample used in measurements[15] between 0.4 and 4°K, This is because the original specimen, when received, was cut into two pieces, the smaller of which was used in the experiments below 4°K and the larger in the present work. The purity of the sample is given in Table I and the specific heat results are listed in Table V and plotted into Fig. 4. An anomaly is again observed, this time at about 17.5°K; the increase in C_p towards temperatures below 4°K is a result of the very large nuclear specific heat of holmium.[15] Altogether six runs were made during which the specimen was warmed to room temperature between runs 4 and 5. Hysteresis effects were carefully looked for at the anomaly but not observed; for instance, the specimen was not cooled below 16.5°K before run 6 was started and cooling over the anomalous region was done at different speeds for different runs.

TABLE V. The specific heat of holmium metal (mJ/mole °K). Experimental results. (At. wt: 164.93 g/mole.)

T	C_p	T	C_p	T	C_p
Run 1		16.772	7958	Run 4	
3.0545	545.7	18.512	8616	11.772	4006
3.2704	508.9	20.510	9920	12.854	4842
3.5281	480.7	22.483	11037	14.055	5821
3.7979	462.9	24.262	12058	15.403	6954
4.0739	458.4			16.894	8114
		Run 3		18.536	8662
Run 2		4.4014	471.7		
3.1423	528.4	4.8322	512.6	Run 5	
3.4022	492.8	5.3828	602.6	14.017	5786
3.6878	469.3	5.9430	735.9	14.661	6307
3.9587	458.4	6.5040	910.7	15.253	6830
4.2846	464.6	7.0924	1135.9	15.804	7283
4.7093	495.7	7.6923	1407.2	16.320	7699
5.1655	558.0	8.3191	1730.1	16.810	8033
5.6606	658.0	9.0147	2122.8	17.283	8242
6.2162	810.9	9.8307	2638.4	17.749	8243
6.7863	1008.3	10.762	3266	18.211	8387
7.3642	1248.2	11.855	4059	18.662	8651
7.9833	1545.6	13.102	5035	19.095	8965
8.6381	1900.6	14.447	6134	19.514	9266
9.3994	2350.6	15.837	7289		
10.302	2933.3	17.276	8174	Run 6	
11.350	3676	19.001	8932	16.542	7823
12.540	4580	20.968	10224	16.855	8163
13.835	5614	22.874	11284	17.158	8333
15.245	6795	24.606	12313	17.457	8399
				17.756	8288

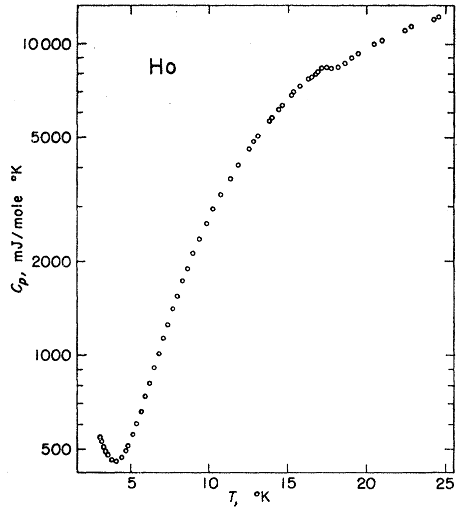

FIG. 4. The specific heat of holmium metal.

Our measurements may be compared with previous experiments by Lounasmaa[15] below 4°K, and by Gordon, Dempesy, and Soller[16] below 14°K. There is agreement to within 0.4% with the former and to about 2% with the latter. A formula, which indicates slightly lower results than ours, has been published by Dreyfus, Goodman, Lacaze, and Trolliet[17] for C_p below 4°K. Above 15°K the present data may be compared with the measurements of Gerstein, Griffel, Jennings, Miller, Skochdopole, and Spedding,[18] who observed a peak at 19.5°K, two degrees above the center of our anomaly. Furthermore, Gerstein *et al.* found their peak to be dependent on the thermal history of the sample, contrary to our observations. Below 17 and above 20°K our results are generally about 2.5% lower than the data of Gerstein *et al.*

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[13] G. Trolliet, thesis, University of Grenoble, 1964 (unpublished).

[14] M. Griffel, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. **25**, 75 (1956).

[15] O. V. Lounasmaa, Phys. Rev. **128**, 1136 (1962).

[16] J. E. Gordon, C. W. Dempesy, and T. Soller, *Rare Earth Research* (Gordon and Breach Publishers, Inc., New York, 1962), p. 203.

[17] B. Dreyfus, B. B. Goodman, A. Lacaze, and G. Trolliet, Compt. Rend. **253**, 1764 (1961).

[18] B. C. Gerstein, M. Griffel, L. D. Jennings, R. E. Miller, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. **27**, 394 (1957).

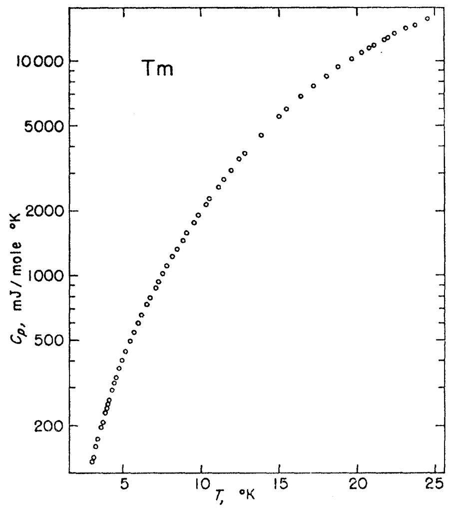

FIG. 5. The specific heat of thulium metal.

5. Thulium

The thulium specimen weighed 48.894 g (=0.28943 moles), slightly less than during the measurements below 4°K [1]; this was mainly because of a few small holes drilled into the sample for obtaining material for chemical analyses. The purity of the metal is again given in Table I and the results of five final runs are listed in Table VI and plotted into Fig. 5. The sample was warmed to room temperature between runs 3 and 4.

The present results yield a specific heat that is completely smooth from 3 to 25°K, but comparison with the previous work of Lounasmaa[1] shows that in the region of overlap, 3 to 4°K, the new data are consistently 3% lower than the old data. This unfortunate situation obviously caused considerable discomfort to us; all possible checks in the measuring equipment and procedures were made, and the second time the sample was brought from room temperature to 3°K only the heat switch was used, whereby the total cooling time became long, about 48 h. However, nothing was found which could explain the discrepancy and runs 4 and 5 gave the same specific heat as runs 1–3. We therefore do not know the cause of the discrepancy, which is further discussed in Sec. V.5.

TABLE VI. The specific heat of thulium metal (mJ/mole °K). Experimental results. (At. wt: 168.93 g/mole.)

T	C_p	T	C_p	T	C_p
Run 1		22.413	13342	9.8488	1903.3
4.3150	290.12	23.715	14854	10.576	2274.9
4.5997	334.4			11.485	2803.1
4.9916	401.3	Run 2		12.496	3485
5.4728	491.7	3.1384	142.58	13.791	4471
6.0048	604.3	3.4313	173.27	15.472	5949
6.5509	733.9	3.7022	205.13	17.211	7652
7.0990	878.5	3.9803	241.42	18.814	9315
7.5989	1026.0			20.312	10952
8.2033	1223.2	Run 3		21.761	12575
8.8488	1462.8	3.3133	160.39	23.155	14184
9.5752	1766.1	3.6316	196.56	24.520	15844
10.354	2146.0	3.8968	230.10		
11.139	2580.9	4.1341	262.67	Run 4	
11.949	3096	4.4588	313.7	3.0715	136.15
12.824	3713	4.7914	367.6	3.3978	169.35
13.832	4503	5.2058	441.6	3.7183	206.82
15.003	5513	5.6998	539.8	4.0453	250.12
16.406	6847	6.2213	655.0		
18.025	8493	6.7507	785.3	Run 5	
19.641	10211	7.2864	934.4	20.794	11459
21.084	11827	7.8525	1107.3	22.000	12835
		8.4647	1318.7	23.280	14323
		9.1356	1582.7		

Our results may be compared with the measurements of Trolliet[13] from 3 to 4°K; his data are 30–40% lower than ours. Further comparison can be made with the results of Jennings, Hill, and Spedding[19] above 15°K. Our points are 20% higher at 15°K, but the two sets of data have converged by the time 25°K is reached. These discrepancies are further discussed in Sec. V.5.

IV. ANALYSIS OF RESULTS

As was mentioned in the Introduction, the main purpose of the present experiments is to obtain some information about the magnetic specific heat. In order to study C_M, it is first necessary to subtract from the observed C_p, the lattice, electronic, and nuclear terms and to eliminate the effects of any anomalies not caused by the metal itself. In this section we discuss the determination of C_L, C_E, and C_N, and also give a summary of the theoretical picture concerning C_M and some related quantities dependent on the magnetic properties of the rare earths. The observed anomalies are discussed in Sec. V.

1. The Electronic and Nuclear Terms

As a first approximation it may be assumed that the conduction electrons in all the trivalent lanthanides behave in a similar manner.[20] From an averaging of the values obtained for C_E in the nonmagnetic metals La,[21,22] Lu,[20] Sc, and Y,[23] it was found that in all cases one could take $C_E=10.5T$ mJ/mole °K, to within ±7% accuracy. In the magnetic rare earths the nuclear specific heat seriously interferes with an accurate determination of C_E, but C_p data for trivalent lanthanides are not in disagreement with the value given above.

The nuclear specific heat is not important in the temperature range considered here, except in the case of holmium, where it has a sizable magnitude up to around 10°K, and to a lesser extent in the case of

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terbium. For these metals, values of C_N found from measurements below 1°K have been used.[9,15,24]

2. The Lattice Specific Heat

The problem of the lattice specific heat C_L, however, is not so readily resolved. It has been possible to obtain a low-temperature Debye Θ for some of the metals by determining the T^3 contribution to C_p below 4°K. In the nonmagnetic metals such a term can be relied on to yield Θ_0, but in the magnetic materials C_M obscures the lattice T^3 contribution, and in addition there are anomalies around 4°K in many cases. It is, moreover, not a particularly good approximation to assume a constant $\Theta=\Theta_0$ throughout the temperature range considered here, since it can be seen from the nonmagnetic rare earths that $\Theta=\text{const}$ between 0 and 4°K, then decreases with increasing temperature, passes through a minimum, and finally levels off at some constant value. Thus, although an average Θ may give reasonable qualitative results on integrated quantities like the entropy over a large temperature interval, for the relatively short range from 3 to 25°K such an approach is bound to be erroneous.

The first procedure that suggests itself in the absence of information on the low-temperature elastic constants, is to assume that the Θ's follow a linear law as a function of atomic weight.[20] Therefore, a series of curves for $\Theta(T)$ were drawn maintaining a linear relationship with the atomic weight by interpolation between the $\Theta(T)$'s of lanthanum[21,22] and lutetium.[20,25] Allowance was also made for the slight variation in the position of the minimum of the Θ versus T curve as one proceeds through the rare-earth series. An estimate of the resulting C_L, using tables of the Debye function by Beattie,[26] quickly revealed that the lattice contributions determined in this way would be excessively large in gadolinium, terbium, and dysprosium in comparison to the measured C_p's and the estimated C_E. In holmium and thulium the results were more promising.

If one considers the problem further it becomes apparent that lanthanum, with a more open lattice structure ($c:a=2\times1.613$) than the rare earths discussed in this paper, is not a very suitable standard for interpolating the Θ's. The heavy lanthanides from gadolinium to thulium, on the other hand, all have lattice parameters strikingly close to those of lutetium (cf. Sec. I). Thus, bearing in mind the observed values $\Theta_0=195$°K for gadolinium (cf. Sec. III1) and $\Theta_0=207$°K for dysprosium (cf. Sec. III3), which are quite close to and within the experimental error from the corresponding value $\Theta_0=210$°K for lutetium, it would seem a reasonable approximation to assume that C_L is the same for all trivalent lanthanides from gadolinium to lutetium.

Table VII. Percentage contributions of C_L, C_E, C_M, and C_N in the total C_p.

Sample	T(°K)	C_L(%)	C_E(%)	C_M(%)	C_N(%)	C_p(mJ/mole °K)[b]
Gd[a]	5	20	31	39	...	180
	10	59	18	23	...	625
	20	77	5	18	...	4470
Tb[a]	5	33	51	7	9	110
	10	64	21	15	<1	590
	20	73	5	22	...	4690
Dy[a]	5	23	35	41	<1	160
	10	60	18	22	...	630
	20	61	4	35	...	5640
Ho	5	7	11	49	33	530
	10	14	4	80	2	2725
	20	36	2	62	...	9550
Tm	5	9	14	77	...	400
	10	19	6	75	...	1990
	20	32	2	66	...	10600

[a] The effects of anomalies have not been removed from C_M.
[b] The values of C_p have been rounded off.

The specific heat of lutetium has recently been measured between 3 and 25°K by Culbert,[25] whose results agree with the data of Lounasmaa[20] in the overlapping region between 3 and 4°K. According to these experiments, the electronic specific heat of lutetium is $11.27T$ mJ/mole °K; this value is not very much different from the previously mentioned average result $C_E=10.5T$ mJ/mole °K for trivalent lanthanides. We have thus assumed

$$\begin{aligned} C_M(\mathrm{X}) &= C_p(\mathrm{X})-C_p(\mathrm{Lu})-C_N(\mathrm{X}) \\ &= C_p(\mathrm{X})-C_L(\mathrm{Lu})-11.27T-C_N(\mathrm{X}), \qquad (1) \end{aligned}$$

where X denotes a heavy rare-earth metal. Thus C_M includes all anomalous contributions to the measured C_p. Table VII gives the percentage contributions of C_L, C_E, C_M, and C_N to the total C_p for the five metals under discussion at 5, 10, and 20°K. Culbert's[25] data have been used in determining the specific heat of lutetium; some values of C_p(Lu) are listed in Table VIII.

Obviously, the major uncertainty in the above calculation of C_M is in our assumption $C_L(\mathrm{X})=C_L(\mathrm{Lu})$; thus in gadolinium and terbium, where the magnetic contribution is quite small compared to C_L, and to some extent in dysprosium also, this effect will be magnified in C_M. In holmium and thulium, on the other hand, where C_M dominates, the uncertainty resulting from our assumption will be considerably less severe.

Table VIII. The specific heat of lutetium metal (mJ/mole °K).[a]

T	C_p	T	C_p	T	C_p
3	39.25	8	250.66	16	2030.5
4	59.38	9	347.1	18	2814.7
5	86.57	10	482.3	20	3693
6	124.93	12	849.6	22	4644
7	178.26	14	1366.9	24	5668

[a] From Culbert, Ref. 25.

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[24] H. van Kempen, A. R. Miedema, and W. J. Huiskamp, Physica 30, 229 (1964).

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3. The Magnetic Specific Heat

After C_M has been determined as discussed above, the final step in the analysis is to find its functional form. At this point we must turn to theory for guidance, and so we shall now digress on the magnetic structures of heavy rare earths and on predictions for the temperature dependence of C_M and of some related properties.

The heavier lanthanides are often referred to as the rare-earth ferromagnets.[27] For most of them we find two magnetic transition temperatures, T_C (ferro- to antiferromagnetic) and T_N (antiferro- to paramagnetic), where $T_C < T_N$. Only holmium[28] and thulium[29] are reported as having T_C within the temperature range considered here [$T_C(\text{Ho}) = 20°\text{K}$, $T_C(\text{Tm}) = 22°\text{K}$]. However, Jennings *et al.*[19] expressed doubts as to whether thullium actually does become ferromagnetic, and this is in spite of indications of a possible transition found from magnetization work by Rhodes, Legvold, and Spedding[29] and by Davis and Bozorth.[30]

It is a well-known fact that the electrons in the incomplete $4f$ shell of the heavy rare-earth metals give rise to the magnetic moments of the ions. However, the resulting magnetic order in the bulk metal, which may involve such complications as indirect exchange via the conduction electrons, anisotropy arising from the crystalline field, etc., is not so readily understood. It would be practically impossible to know where to start one's theory without the aid of x-ray diffraction, which indicates the crystal structure, and without the even more powerful tool of neutron diffraction. The latter can be used to determine the type of magnetic ordering in a metal, and also the magnitude of the ordered moments. Once these facts are known it becomes possible perhaps to predict the observed behavior of the magnetic properties as evidenced in magnetic susceptibility, magnetic specific heat and the magnon contribution to the electrical resistivity.[31]

The magnetic structures of heavy rare earths have been studied notably by the research group at the Oak Ridge National Laboratory. The observed magnetic ordering can be classified according to several types of anisotropy, in which there is a marked difference between the magnitudes of the moments in the direction of the hexagonal axis and at right angles to it. First, there is the type found for terbium and dysprosium in the ferromagnetic state, where the moments are all parallel and lie in the basal plane (i.e., basal anisotropy). Secondly, we find what is known as the antiferromagnetic spiral, or simple-spiral spin structure (SS); this is displayed, within the temperature range studied here, in modified form by holmium (cf. Sec. V.4). In the simple spiral the magnetic moments lie in the basal plane, parallel within the plane, but lying at an angle relative to each other in successive layers. Thus, looking along the direction of the hexagonal axis, we observe a simple-spiral structure in which the moments in each layer make a turn angle α with those in the neighboring layers. It is found that α generally decreases linearly with decreasing temperature until it reaches some constant value or the metal undergoes a magnetic transition.

Finally, we are here concerned with the ferromagnetic spiral (FS), which is observed in holmium (and erbium). Below T_C in the ferromagnetic state the magnetic moments lie on the surface of a cone generated around the hexagonal axis. The components in the basal plane form the simple spiral described above and do not have a resultant moment. Thus the net moment of the metal depends on the components along the hexagonal axis. The cone half-angle ϑ changes with temperature.

Gadolinium and thulium are special cases; the former will be discussed later in this section, the latter in Sec. V.5.

We are now in a position to investigate briefly, on the basis of the above outline, several theoretical models proposed for explaining the interrelationships between the magnetic structure and various other properties of the rare-earth metals.

The simple spin-wave theory[32] assumes a purely isotropic Hamiltonian for the magnetic spin system, which is approximated formally by an assembly of harmonic oscillators. A magnon or spin-wave frequency spectrum, $\hbar\omega(\mathbf{q})$, is then obtained and from this one can calculate the various statistical properties of interest. For a ferromagnet $\omega(\mathbf{q}) \sim \mathbf{q}^2$, and the deviation ΔM of the total magnetic moment M_z in the direction of the applied field from its maximum value M_{z0} achieved at $T=0$, is given by the Bloch law

$$\Delta M = M_{z0} - M_z = \text{const}(kT)^{3/2}. \qquad (2)$$

The constant of proportionality depends on the lattice symmetry, but the $T^{3/2}$ law is valid for any three-dimensional lattice. The spin-wave contributions to the specific heat and electrical resistivity are given by

$$C_M = \text{const}(kT)^{3/2} \quad \text{and} \quad \rho_M = \text{const}(kT)^2. \qquad (3)$$

In an antiferromagnet at low temperatures and in the long wavelength limit, it is found that the dispersion relation is linear, i.e., $\omega(\mathbf{q}) \sim \mathbf{q}$. The corresponding

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[27] For reviews of the magnetism of the rare earth metals see: K. P. Belov, R. Z. Levitin, and S. A. Nikitin, Usp. Fiz. Nauk **82**, 449 (1964) [English transl.: Soviet Phys.—Usp. **7**, 179 (1964)]; R. J. Elliott, in *Magnetism IIA*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), p. 385.

[28] S. Legvold, *Collected Rare Earth Research* (Macmillan and Company, Inc., New York, 1961), p. 142.

[29] B. L. Rhodes, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1547 (1958).

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[31] See, for example, R. J. Elliott, Phys. Rev. **124**, 346 (1961) and reviews given in Ref. 27.

[32] J. Van Kranendonk and J. H. Van Vleck, Rev. Mod. Phys. **30**, 1 (1958) and references given therein.

results are then

$$\Delta M=\mathrm{const}(kT)^2,\quad C_M=\mathrm{const}(kT)^3,$$
and
$$\rho_M=\mathrm{const}(kT)^4. \tag{4}$$

In 1960 Niira[33] produced a theory which explained why ΔM in dysprosium (and in terbium) in the ferromagnetic state at low temperatures deviates markedly from the Bloch $T^{3/2}$ law of Eq. (2). Niira's model shows that, if there is a preferred direction of magnetization in the crystal because of magnetic anisotropy, a finite amount of energy is required to excite even a long-wavelength spin wave. Niira considers the hcp lattice as being composed of two interpenetrating hexagonal sublattices. Anisotropy is mainly introduced by the crystalline field which acts on each magnetic ion, and the spin-wave spectrum can be derived from the total Hamiltonian of exchange and crystalline energies. The two sublattices introduce two branches in the spin-wave dispersion spectrum; the higher branch, which corresponds to the optical mode of coupling between the two sublattices, is neglected. Then, for sufficiently low temperatures, Niira obtains the approximation

$$\Delta M=\mathrm{const}(kT)^{3/2}\sum_{n=1}^{\infty}(e^{-nx}/n^{3/2}), \tag{5}$$

where $x=JK/kT$; here J is the total angular momentum of the ion and K is an energy defined by Niira (K corresponds to Δ in Niira's notation). The sum in Eq. (5) has a roughly exponential dependence on $1/T$. Moreover, since JK is approximately the geometrical mean of the magnetic anisotropy for the c direction (K_2) and for the $[11\bar{2}0]$ direction (K_6), the low-temperature behavior of the magnetization in an hcp crystal can be given qualitatively by

$$\Delta M=\mathrm{const}(kT)^{3/2}\exp(-E_g/kT), \tag{6}$$

where $E_g=(K_2K_6)^{1/2}$, equal to the minimum energy required to excite a spin-wave in the presence of the anisotropy field.

The corresponding results for specific heat and electrical resistivity are

$$C_M=\mathrm{const}(kT)^{3/2}\exp(-E_g/kT)$$
and
$$\rho_M=\mathrm{const}(kT)^2\exp(-E_g/kT). \tag{7}$$

Gadolinium with the $4f$ shell half-filled is a special case. Since the ground state of the Gd^{3+} ion is $^8S_{7/2}$, there is no orbital moment and hence no L-S coupling, which in the other rare earths is responsible for the strong interaction of the magnetic spin moment with the crystalline field. Thus, to a first approximation the gadolinium ions have a very small anisotropy in the metal. This means that E_g/k is small, which leads us from Eqs. (6) and (7) to the simple Bloch law given in Eqs. (2) and (3). If, on the other hand, the anisotropy in the basal plane vanishes completely, this affects the crystalline field Hamiltonian in such a manner that the spin-wave spectrum becomes linear in the wave vector $\mathbf{q}$ and we would obtain the results given by Eqs. (4).

The third theory with which we are concerned is that of Kaplan,[34] who showed that the simplest Hamiltonian that has hexagonal symmetry, and which will give rise to a ferromagnetic spiral (FS) as the ground state, must include terms of at least the fourth power in the spin variables $\mathbf{S}_i$. The necessary conditions for a stable minimum energy imply that the second-order terms in $\mathbf{S}_i$ must provide an easy axis of magnetization, and the fourth-order terms must give an easy plane in order to produce a ferromagnetic spiral. Employing the usual harmonic-oscillator approximation the spin-wave spectrum can be found, and at low temperatures, for sufficiently small $\mathbf{q}$, $\hbar\omega(\mathbf{q})=\mathrm{const}\mathbf{q}$. Thus Kaplan has shown that a basically ferromagnetic configuration can give a linear dispersion law, which is normally associated with antiferromagnetism as manifested in Eqs. (4) above. This result can be explained by observing that the normal frequency modes correspond approximately to oscillations of the components perpendicular to the magnetization, these moments themselves forming a simple antiferromagnetic spiral. If an energy gap arises from the introduction of anisotropy,[34] then one would obtain, as was pointed out by Mackintosh,[35]

$$\Delta M=\mathrm{const}(kT)^2\exp(-E_g/kT),$$
$$C_M=\mathrm{const}(kT)^3\exp(-E_g/kT),$$
and
$$\rho_M=\mathrm{const}(kT)^4\exp(-E_g/kT). \tag{8}$$

Finally, Cooper[36] has presented a model initially intended to describe the magnetic specific heat of dysprosium. According to his theory, at low temperatures, where $kT\ll E_g$, $C_M\sim(E_g/kT+2+2kT/E_g)\times\exp(-E_g/kT)$. However, he admits that the factor multiplying the exponential is not exact in view of the approximations made in the spin-wave spectrum. This formula cannot be expected to hold for the temperature interval presently under study, since $kT\ll E_g$ implies, by assuming $E_g/k=30°\mathrm{K}$ (see Sec. V.3), $T<E_g/10k=3°\mathrm{K}$. For $T\geqslant E_g/k$ Cooper[36] predicts $C_M\sim T$, but this temperature range was not reached in our work. The most consistent analysis of the present data will thus be obtained if we bear in mind the theoretical calculations presented earlier in this section.

V. DISCUSSION

1. Gadolinium

After subtracting C_L and C_E, several graphs of C_M versus T were made; two of them are shown in Fig. 6.

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[34] T. A. Kaplan, Phys. Rev. **124**, 329 (1961); see also, A. Yoshimori, J. Phys. Soc. Japan **14**, 807 (1959).

[35] A. R. Mackintosh, Phys. Letters **4**, 140 (1963).

[36] B. R. Cooper, Proc. Phys. Soc. (London) **80**, 1225 (1962).

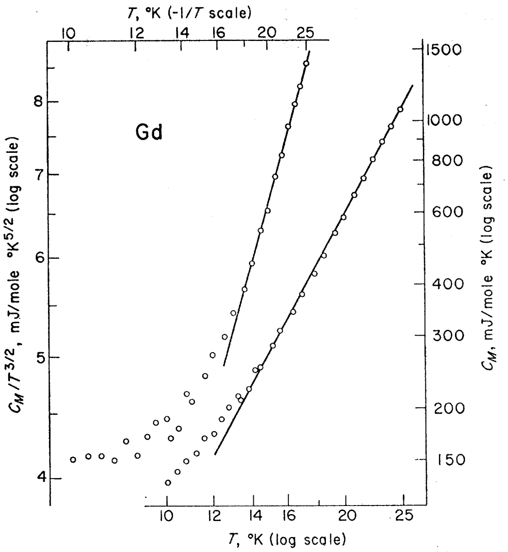

FIG. 6. The magnetic specific heat of gadolinium metal plotted as log $C_M/T^{3/2}$ versus $-1/T$ (left and top scales) and as log C_M versus log T (right and bottom scales). The straight lines correspond to the relations $C_M = 24T^{3/2}\exp(-26/T)$ mJ/mole°K and $C_M = 0.19T^{2.7}$ mJ/mole°K, respectively.

The log C_M versus log T plot indicates no clear power law applicable to the whole temperature range above the low-temperature anomaly. It would, however, be possible to write $C_M = 0.19T^{2.7}$ mJ/mole°K between 13 and 25°K. An attempt to find an exponential fit was equally unconvincing, although above 18°K we could possibly write $C_M = 24T^{3/2}\exp(-26/T)$ mJ/mole°K; powers of 1, 2, and 3 were also tried for T but with even less success. Bearing in mind that the lattice specific heat is a large percentage of the total C_p (cf. Table VII), so that any error in our estimation of C_L will be considerably magnified in C_M, we cannot hope to make a detailed numerical analysis of the functional form of the magnetic specific heat. We must, instead, look for other experimental evidence to help us in making a selection.

There are data in favor of a T^3 temperature dependence of C_M of gadolinium metal. Neutron diffraction work by Will, Nathans, and Alperin,[37] admittedly only above 77°K as yet, indicates that gadolinium behaves as a normal ferromagnet and will not display helical antiferromagnetism (SS), nor presumably helicoidal ferromagnetism (FS). Recent measurements by Nigh, Legvold, and Spedding,[38] and by Colvin and Arajs[39] show that the magnetization and electrical resistivity behave, from the ferromagnetic Curie temperature $T_C = 290$°K down to about 50°K, according to the predictions of the simple spin-wave theory, i.e., $\Delta M \sim T^{3/2}$ and $\rho_M \sim T^2$. Below 50°K there is a departure from these laws[39a] and one finds approximately $\Delta M \sim T^2$ and $\rho_M \sim T^4$; these relations are in agreement with Eqs. (4). Magnetic studies of gadolinium[40–43] have revealed a small c-axis anisotropy and a negligible basal anisotropy. If the latter could indeed be considered as nonexistent we would obtain from Niira's[33] theory, as applied to gadolinium (cf. Sec. IV.3), a linear spin-wave dispersion law and thus the behavior given in Eqs. (4), i.e., $C_M \sim T^3$, in close agreement with our experimental result $C_M \sim T^{2.7}$ and in accord with the measurements of Nigh *et al.*[38] and of Colvin and Arajs.[39]

There is also evidence in favor of an exponential temperature dependence of C_M. In low fields Nigh *et al.*[38] observed a small basal anisotropy, which was, however, within the limit of experimental error. If such anisotropy did exist we would once again obtain the exponential temperature dependences of Eqs. (6) and (7). In agreement with this Rode, Herrmann, and Korolev[44] found that between 4.2 and 30°K the saturation magnetization may be written $\Delta M = \mathrm{const}(kT)^{3/2} \times \exp(-30/T)$.

On the basis of the foregoing discussion it appears to us that experimental evidence is stronger in favor of a T^3 than of an exponential temperature dependence of the magnetic specific heat of gadolinium. We thus tentatively write (in mJ/mole °K)

$$C_M = 0.19T^{2.7}. \tag{9}$$

This relation represents our experimental data between 13 and 25°K whereas an exponential expression would cover only the range from 18 to 25°K (cf. Fig. 6), which is further evidence in favor of a simple power law for C_M.

Finally, a few remarks about the anomaly at 3.7°K. We assume that it is due to gadolinium sesquioxide, Gd_2O_3, especially in view of the measurements by Crane,[6] by Donald *et al.*,[7] and by Lounasmaa[5] on samples with various oxygen contents, as was discussed in Sec. III.1. Justice and Westrum,[45] in studies of Gd_2O_3, found that the ground state of Gd^{3+} ions ($^8S_{7/2}$) is split by the crystalline field into a quartet flanked by two doublets. However, the various inaccuracies involved make difficult a reliable comparison of the entropy arising from such a level scheme and the observed

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[38] H. E. Nigh, S. Legvold, and F. H. Spedding, Phys. Rev. **132**, 1092 (1963).

[39] R. V. Colvin and S. Arajs, Phys. Status Solidi **4**, 37 (1964).

[39a] *Footnote added in proof.* More recent measurements by M. Nielsen (private communication) indicate that the $T^{3/2}$ dependence of the magnetic susceptibility of Gd continues below 50°K down to 4°K.

[40] S. Arajs, and R. V. Colvin, J. Appl. Phys. Suppl. **32**, 336S (1961).

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[43] J. F. Elliott, S. Legvold, and F. H. Spedding, Phys. Rev. **91**, 28 (1953).

[44] V. E. Rode, R. Herrmann, and L. M. Korolev, Zh. Eksperim. i Teor. Fiz. **46**, 1507 (1964) [English transl.: Soviet Phys.—JETP **19**, 1021 (1964)].

[45] B. H. Justice and E. F. Westrum, Jr., J. Phys. Chem. **67**, 345 (1963).

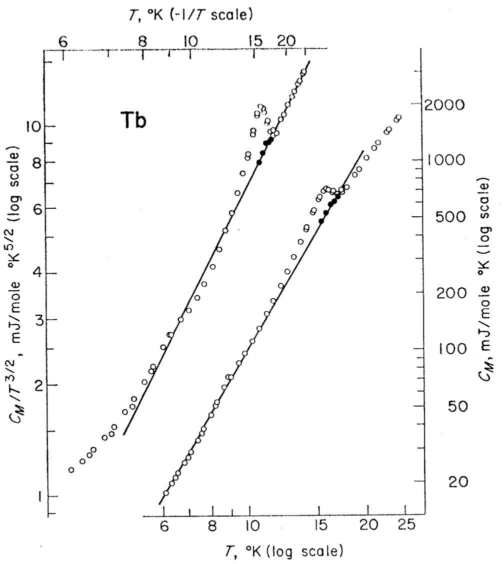

FIG. 7. The magnetic specific heat of terbium metal; filled circles are points from run 5. The straight lines correspond to the relations $C_M=36T^{3/2}\exp(-23.5/T)$ mJ/mole°K (on the left) and $C_M=0.031T^{3.5}$ mJ/mole°K (on the right).

entropy under the peak. It appears, however, that in order to achieve the expected entropy, either the peak extends to about 10°K or some of the oxygen is distributed interstitially into the metal and not collected into oxide pockets, whereby it does not partake in the anomalous entropy.

2. Terbium

In calculating the magnetic specific heat of terbium the nuclear term must be taken into account, thus Eq. (3) in Ref. 9 was used for determining C_N. Figure 7 shows on the left a plot of $\log(C_M/T^{3/2})$ versus $-1/T$. It may be seen, if we discount the effects of the anomaly around 16°K by using points from run 5 (cf. Sec. III.2), that a fairly good fit is given by $C_M=36T^{3/2}\times\exp(-23.5/T)$ mJ/mole°K. It is, however, shown on the right of Fig. 7 that one could almost equally well write $C_M=0.031T^{3.5}$ mJ/mole°K. This inconclusive situation can be resolved by examining the magnetic structure of terbium and related theoretical predictions.

According to Koehler, Child, Wollan, and Cable[46] terbium in the ferromagnetic region at low temperatures exhibits strong uniaxial anisotropy with the easy direction of magnetization lying in the basal plane. Thus according to the outline in Sec. IV.3, we would expect agreement with Niira's[33] theoretical result for an anisotropic ferromagnet, i.e.,

$$C_M\sim T^{3/2}\exp(-E_g/kT).$$

Unfortunately we cannot immediately accept this conclusion, since Arajs and Colvin[47] found that between 5 and 20°K the intrinsic resistivity of terbium has a $T^{4.2}$ temperature dependence, as opposed to $\rho_M\sim T^2\times\exp(-E_g/kT)$ corresponding to Niira's theory. However, Arajs and Colvin neglected the electron-phonon and electron-electron resistivities and so their result should not be stressed in the present connection. The relation $C_M\sim T^{3.5}$ has no theoretical justification. Thus, until further work perhaps proves to the contrary, we conclude that, in agreement with Niira's[33] theory, our measurements give (in mJ/mole °K)

$$C_M=36T^{3/2}\exp(-23.5/T) \qquad (10)$$

for the magnetic specific heat of terbium.

There is, at the present time, no explanation of the hysteresis phenomenon observed between 14.5 and 17°K (cf. Fig. 2). The entropy enclosed by the loop is approximately 20 mJ/mole °K. The anomaly is most likely connected with the magnetic behavior of the bulk metal.

Nor can much be said about the peak at 4.5°K. Since the entropy associated with the anomaly is much smaller than the theoretical value expected from crystalline field splitting in the oxide, it is possible that some other impurity is involved. Moreover, heat-capacity measurements by Stanton, Jennings, and Spedding[48] and susceptibility data by Gerstein, Jelinek, and Spedding[49] show that antiferromagnetic ordering occurs in Tb_2O_3 at 2.4°K.

3. Dysprosium

The specific-heat curve for dysprosium exhibits an anomalous peak at 5°K and therefore the analysis to determine the magnetic contribution was done for $T>7$°K. As is shown in Fig. 8, a good fit was obtained for $C_M=107T^{3/2}\exp(-31/T)$ mJ/mole °K. This result is in agreement with Niira's[33] theory, which is applicable to dysprosium on account of the strong uniaxial anisotropy in the basal plane. According to Wilkinson, Koehler, Wollan and Cable,[50] the magnetic structure of dysprosium, with transition temperatures $T_C=85$°K and $T_N=179$°K, is very similar to that of terbium. The same arguments can thus be applied to both metals. Niira predicted $E_g/k=20$–40°K for dysprosium; our experimental value 31°K is in the middle of this range. Flotow and Osborne[11] obtained a quite different result, $E_g/k=53$°K, although their C_p data coincide with ours between 8 and 25°K (cf. Sec. III.3). The essential differences between the analyses are that Flotow and Osborne used an estimated Debye Θ of 186°K to

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[46] W. C. Koehler, H. R. Child, E. O. Wollan, and J. W. Cable, J. Appl. Phys. **34**, 1335 (1963).

[47] S. Arajs and R. V. Colvin, Phys. Rev. **136**, A439 (1964).

[48] R. M. Stanton, L. D. Jennings, and F. H. Spedding, J. Chem. Phys. **32**, 630 (1960).

[49] B. C. Gerstein, F. J. Jelinek, and F. H. Spedding, Phys. Rev. Letters **8**, 425 (1962).

[50] M. K. Wilkinson, W. C. Koehler, E. O. Wollan, and J. W. Cable, J. Appl. Phys. Suppl. **32**, 48S (1961).

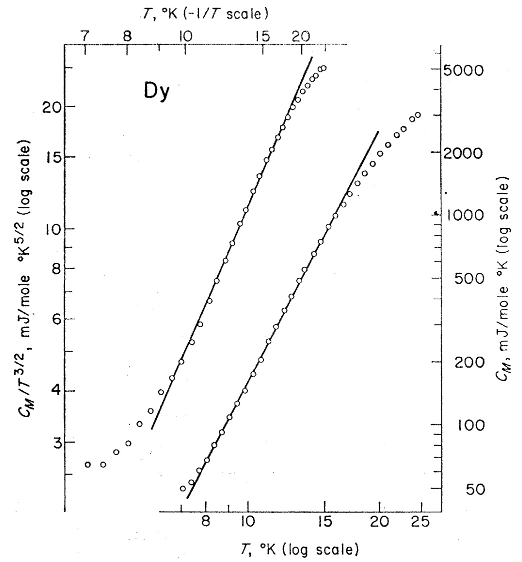

FIG. 8. The magnetic specific heat of dysprosium metal. The straight lines correspond to the relations $C_M = 107T^{3/2}\exp(-31/T)$ mJ/mole°K (on the left) and $C_M = 0.016T^{4.0}$ mJ/mole°K (on the right).

describe the lattice specific heat for the whole range, which procedure we have avoided for reasons discussed in Sec. IV.2, and that they followed the formula of Cooper's[36] theory, which we have shown in Sec. IV.3 to include approximations not justified in the temperature range presently under investigation.

It would thus appear that the exponential term is verified experimentally, except that, as for terbium, we can again obtain an equally good fit to a simple power law, $C_M = 0.016T^{4.0}$ mJ/mole°K, as shown in Fig. 8. We thus must consider the experimental and theoretical evidence together, and on the same grounds as discussed in the previous section, we conclude (in mJ/mole °K)

$$C_M = 107T^{3/2}\exp(-31/T). \qquad (11)$$

An exponential term also adequately accounts for the behavior of magnetization at low temperatures.[51,52]

The peak at 5°K (cf. Fig. 3) is of Schottky type. The entropy associated with it is again smaller, even when the anomaly at 2.3°K is also taken into account,[3] than expected from splitting of the ground state of dysprosium by the oxide crystalline field.[53] Below 4.2°K Brown and Hubbard[54] in measurements of the magnetic susceptibility of Dy_2O_3 found no evidence for magnetic ordering. On the other hand, differences in the specific heat of the present specimen and that used by Dreyfus *et al.*,[12] as discussed in Sec. III.3, show that the oxide impurity is of importance here. Further measurements are necessary for resolving this dilemma.

4. Holmium

In holmium the nuclear specific heat is sizeable up to 10°K (cf. Table VII) and thus C_N, calculated from the data by Lounasmaa,[15] must be taken into account in determining C_M. It should be recalled also that in holmium the magnetic contribution dominates in C_p and so any errors in the estimated lattice specific heat will have a smaller effect in C_M than for the previous three metals.

The log C_M versus log T plot in Fig. 9 shows that the relation $C_M = 1.5T^{3.2}$ mJ/mole°K is quite accurately valid between 3 and 9°K. Above 9°K the transition culminating in the peak at 17.5°K begins to have an effect. We also investigated whether an exponential temperature dependence of C_M would fit our data: plots of log (C_M/T^n) versus $-1/T$ for $n=1$, $\frac{3}{2}$ (cf. Fig. 9), 2, and 3 were made, but the agreement was never satisfactory, since the marked deviations observed in such plots below 5°K cannot be excused by a low-temperature anomaly, as in the cases of terbium and dysprosium.

Koehler, Cable, Wollan, and Wilkinson[55] found from their neutron-diffraction studies of holmium that at 4.2°K the magnetic moments form a ferromagnetic spiral with cone half-angle $\vartheta \sim 78$°K and turn angle $\alpha = 30°$. Thus holmium's magnetic structure is inter-

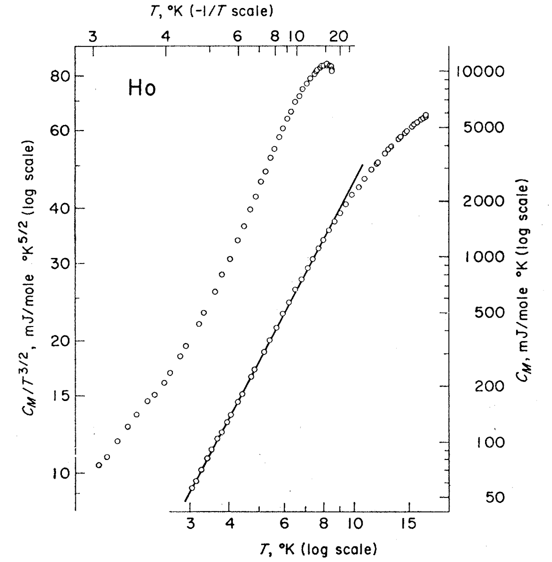

FIG. 9. The magnetic specific heat of holmium metal. The straight line corresponds to the relation $C_M = 1.5T^{3.2}$ mJ/mole °K.

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[51] D. R. Behrendt, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1544 (1958).

[52] J. F. Elliott, S. Legvold, and F. H. Spedding, Phys. Rev. **94**, 1143 (1954).

[53] E. F. Westrum and B. H. Justice, J. Phys. Chem. **67**, 659 (1963).

[54] R. E. Brown and W. M. Hubbard, Proceedings of the 5th Rare Earth Research Conference, Ames (1965), Part 4, p. 31, (unpublished).

[55] W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, J. Phys. Soc. Japan Suppl. **17**, 32S (1962).

mediate between dysprosium and erbium, the two metals considered by Kaplan.[34] Therefore, for the ferromagnetic state of holmium we would expect a linear spin-wave dispersion law which gives C_M proportional to T^3 [cf. Eq. (4)]. Measurements by Strandburg, Legvold, and Spedding[56] suggest $\rho_M = \mathrm{const}(kT)^4 \times \exp(-E_g/kT)$, where E_g has not been determined but is small.[35] If $E_g/k \ll T$, we would get $\rho_M = \mathrm{const}(kT)^4$, in agreement with the above proposal for C_M. Finally, Strandburg *et al.*[56] showed that below 20°K one may write $\Delta M = \mathrm{const}(kT)^2$, although a $T^{3/2}$ temperature dependence was not ruled out.

In view of the above discussion we conclude that the magnetic specific heat of holmium, below 8°K, can be written (in mJ/mole °K)

$$C_M = 1.5T^{3.2}. \tag{12}$$

The temperature dependence is close to Kaplan's[34] prediction $C_M \sim T^3$.

Our specific heat curve (cf. Fig. 4) shows a small peak with its maximum at 17.5°K. As was discussed in Sec. III.4, the height of our anomaly was not dependent on the thermal history of the sample in contrast to the observations of Gerstein *et al.*[18] The excess entropy due to the peak, which apparently covers the temperature range from approximately 9 to 18.2°K (cf. Fig. 9), is of the order of 280 mJ/mole°K. Strandburg *et al.*[56] found that a slight change in the slope occurred at 20°K in the electrical resistivity curve. As the temperature is decreased, the turn angle, which remains constant at $\alpha = 36°$ between 35°K and about 20°K, undergoes an abrupt decrease to 30° near 20°K. This is possibly due to an increase in the anisotropy along the $[10\bar{1}0]$ directions.[55,56] However, this change is accompanied by a tilting of the moments out of the basal plane to give a cone half-angle $\vartheta = 78°$ so that although the true interplanar angle is decreased slightly, the magnetic component in the basal plane shows no change.[57] Thus the small amount of entropy is attributed to a phase change involving only this rearrangement of the spin magnetic moments near 20°K, although in our case the transition seems to occur nearer to 17°K.

5. Thulium

The magnetic structure of thulium is somewhat dissimilar from that of the other rare earths previously dealt with. Neutron diffraction measurements by Koehler, Cable, Wollan, and Wilkinson[58] on single crystals have shown that thulium is paramagnetic above $T_N = 56°$K, below which the spin structure corresponds to a moment varying sinusoidally along the c axis. The period of modulation is $3.5c$ and remains constant down to about 40°K, at which temperature there are indications of a slight change in magnetic ordering so that there is a net ferromagnetic moment arising from a $+4, -3, +4, -3, \cdots$ sequence. This has been convincingly demonstrated[58] at 4.2°K. It would appear that this type of structure is not amenable to treatment by the simple spin-wave theory. Apart from some work by Elliott and Wedgwood,[59] who really considered only the turn angle as a function of temperature, there are no adequate theoretical predictions on the temperature behavior of the magnetic specific heat of thulium.

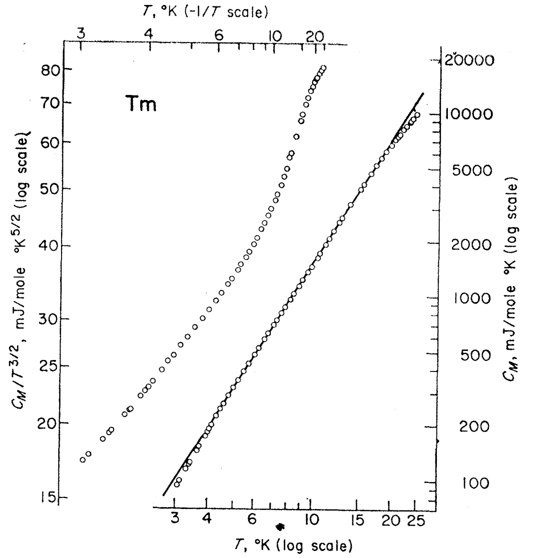

FIG. 10. The magnetic specific heat of thulium metal. The straight line corresponds to the relation $C_M = 8.3T^{2.3}$ mJ/mole °K.

Our C_p curve (cf. Fig. 5) is smooth over the whole temperature range presently under investigation. We find from the log C_M versus log T plotted in Fig. 10 that $C_M = 8.3T^{2.3}$ mJ/mole°K from 4 to 20°K. This result should be fairly reliable since, as may be seen from Table VII, the magnetic specific heat is by far the largest contribution in the observed C_p of thulium. Our present result agrees quite well with $C_M = 6.2T^{2.5}$ mJ/mole°K found previously from specific-heat data[1] below 4°K.

Magnetization measurements[29,30] have indicated a Curie point near 20°K and there is also evidence[29,60] of a maximum in the magnetic moment at 12°K. Differences between the various specific-heat data (cf. Sec. III.5) almost certainly point to a magnetic transformation that is dependent on the detailed microstructure, thermal history or impurity content of the specimens. The good power law fit we found for C_M shows, however, that the anomaly is spread out over a wide temperature range. The slight deviation of C_M from the $T^{2.3}$ temperature dependence above 20°K (cf. Fig.

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[56] D. L. Strandburg, S. Legvold, and F. H. Spedding, Phys. Rev. **127**, 2046 (1962).

[57] F. J. Darnell, Phys. Rev. **130**, 1825 (1963).

[58] W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **126**, 1672 (1962).

[59] R. J. Elliott and F. A. Wedgwood, Proc. Phys. Soc. (London) **84**, 63 (1964).

[60] W. E. Henry, J. Appl. Phys. Suppl. **31**, 323S (1960).

10) indicates that the anomaly is possibly centered somewhere near this temperature in agreement with magnetization measurements.[29,30]

In the absence of theoretical guidance and contradictory experimental evidence, we write for thulium below 20°K (in mJ/mole °K)

$$C_M=8.3T^{2.3}. \tag{13}$$

6. Impurity Effects

Considerable discrepancies, as discussed in Sec. III, were observed between the specific-heat data of different investigators. In general, agreement is found in nonanomalous regions and disagreement near the various peaks. It is fairly clear that the low-temperature discrepancies are caused by impurities, the culprits being, at least in some cases, the sesquioxides. Other impurities may not be ruled out, since measurements of the magnetic susceptibility by Brown and Hubbard[54] showed that in several cases a magnetic transformation does not take place in the oxide at a temperature where there is a specific-heat anomaly in the corresponding metal. Dreyfus *et al.*,[12] who investigated the specific heat of dysprosium, and Colvin and Arajs,[61] who studied the electrical resistivity of rare-earth metals, made the proposition that tantalum contamination (the metals are normally cast in tantalum crucibles), causes the low temperature anomalies they found in these properties. The present work does not support this view because in our terbium sample no tantalum was detected and in dysprosium the amount of this impurity was only 0.026% (cf. Table I), which is lower than the tantalum concentration in that sample of Dreyfus *et al.* which did not exhibit an anomaly below 4°K (cf. Sec. III.3). Moreover, thulium, which of all our specimens contains the highest percentage of tantalum, shows no anomaly at low temperatures.

VI. CONCLUSIONS

Determination of the magnetic specific heat from our measurements rests on the assumption that, on account of the similarity of their lattice constants and their outer electronic configuration, the lattice and electronic specific heats of the higher trivalent rare earths are the same, i.e., we can use the known C_L and C_E of lutetium for all these metals. There is, at present, no way of estimating the errors introduced in this way, except that those arising from C_E are relatively small because this contribution in itself is small. Considerable difficulties in the analysis are also caused by several irregularities in the observed C_p. The high-temperature anomalies in terbium and holmium are apparently associated with magnetic transformations in the metals themselves whereas the low-temperature peaks observed for gadolinium, terbium, and dysprosium are probably attributable to impurities.

We have found two different types of behavior for C_M of the heavy rare earths. In terbium and dysprosium there is evidence for an exponential temperature dependence; these two metals show strong basal anisotropy in their magnetic properties, and in agreement with Niira's[33] theory we find $C_M\sim T^{3/2}\times\exp(-E_g/kT)$. For the remaining metals simple power laws were observed. In gadolinium $C_M\sim T^{2.7}$, in close agreement with Niira's prediction $C_M\sim T^3$. For holmium we find $C_M\sim T^{3.2}$, which is in accord with the T^3 law predicted by Kaplan[34] for a ferromagnetic spiral spin structure. For thulium we obtain $C_M\sim T^{2.3}$; there are no theoretical predictions in this case, but in view of the almost ferrimagnetic structure of thulium such a temperature dependence is not ruled out. For most of these metals the observed behavior of C_M can be correlated with existing data on magnetization and electrical resistivity.

In fitting the magnetic specific heats to mathematical expressions, we have constantly been guided by modern theories. It is quite possible that purely empirical formulas would represent C_M with higher precision; the value of such formulas is, however, marginal.

The partial lack of agreement between measurements of C_p by various investigators is of some concern. We conclude that above 10°K the discrepancies, observed notably for terbium, holmium, and thulium, are traceable to hysteresis effects in the magnetic structures of the specimens, even though it has been possible to demonstrate these effects only in a few cases. Despite the differences, the temperature dependence found for C_M is of significance, but its absolute magnitude is of lesser importance. The low-temperature discrepancies are clearly attributable to differences in the impurity contents of the specimens.

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