harmonic power. This power can then be found either in the unseparated beam transmitted in a plane parallel slab, one coherence length thick, or in separated beams after passage through a prism. A similar state of affairs applies if one tries to separate the homogeneous and inhomogeneous rays in the focal points of a chromatic lens.

The incorporation of the electromagnetic nonlinearities of matter into Maxwell's equations has led to the solution of a number of simple boundary problems. The reflection and refraction at the surfaces of nonlinear dielectrics makes it possible to analyze the generation and degeneration of light harmonics and mixing of light waves when nonlinear media occur in the optical path. This is important for the understanding of the operation of optical instruments and optical systems at very high power densities available in laser beams.

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Specific Heat of Terbium Metal between 0.37 and 4.2°K*

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The specific heat C_p of terbium metal, measured between 0.37 and 4.2°K in a He^3 cryostat, could be separated by a least squares analysis into three contributions: the lattice specific heat $C_L=0.58T^3$ (corresponding to a Debye $\theta=150$°K), the electronic specific heat $C_E=9.05T$, and the nuclear specific heat $C_N=238T^{-2}-11.9T^{-3}-4.5T^{-4}+0.38T^{-5}+0.06T^{-6}$ (C_p in mJ/mole °K). C_N is due to the splitting of the nuclear spin states by the magnetic field H_{eff} of the $4f$ electrons and by the nuclear electric quadrupole coupling. In the series expansion for C_N there are only two independent constants, the magnetic hyperfine constant a' and the quadrupole coupling constant P. Our experimental values of $a'=0.150$°K and $P=0.021$°K are in good agreement with results obtained by electron paramagnetic resonance and nuclear magnetic resonance techniques which gave $a'=0.152$°K and $P=0.029$°K. By assuming $\mu=1.52$ nuclear Bohr magnetons for Tb^{159} one obtains $H_{\mathrm{eff}}=4.1$ MG. In sharp contrast with earlier results, our measurements revealed no anomalies in C_p between 1 and 4°K. Such anomalies thus were probably caused by impurities in the samples of the other investigators.

I. INTRODUCTION

BELOW 1°K the specific heat of terbium shows a large rise due to the magnetic hyperfine interaction between the $4f$ electrons and the magnetic moment of the nucleus. In addition to this, Bleaney and Hill[1] and Bleaney[2] have shown that the effect of nuclear electric quadrupole coupling might be of importance in calculating the nuclear specific heat of some rare earths, including terbium. The first heat capacity measurements on terbium in the liquid-helium range were performed by Kurti and Safrata[3] between 0.5 and 6°K. Recently, Heltemes and Swenson[4] have used a magnetic refrigerator cryostat to measure the heat capacity between 0.25 and 1°K. Both results are in reasonably good agreement and show the very large increase in specific heat below 1°K.

In order to determine experimentally from heat capacity measurements whether a quadrupole interaction is present, it is necessary to have accurate data at as low temperatures as possible. Bleaney and Hill[1] have analyzed the results of Heltemes and Swenson[4] and found support for the presence of a quadrupole interaction, but, because of scatter of the experimental points and possible systematic error of 10% at the lowest temperatures, this was somewhat inconclusive. It was for this reason that we decided to measure the specific heat of terbium below 1°K.

Above 1°K, the experimental points of Kurti and Safrata[3] showed considerable scatter and an apparent broad anomaly in the heat capacity between 1 and 4°K. Later measurements by Stanton, Jennings, and Spedding[5] between 1.4 and 4°K and by Bailey[6] between 1.7 and 4°K revealed a λ-type anomaly in the specific heat at about 2.3°K, but the two results did not agree with each other nor with the data of Kurti and Safrata. Differences of more than 100% were observed at 4°K. In view of this confusion, we continued our measurements up to 4°K.

The nuclei of many rare earths find themselves in a

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strong effective magnetic field H_{eff} (Marshall,[7] Kondo[8]) which arises mainly from the orbital angular momentum of the $4f$ electrons. In addition, a considerable electric field gradient, parallel to H_{eff} because of the strong coupling between the spin and orbit, can also be expected at the nucleus. The Hamiltonian for the nuclei will thus become[1,2]

$$\mathcal{H}=a'I_z+P[I_z^2-\tfrac{1}{3}I(I+1)], \qquad (1)$$

where the magnetic field is in the z direction. The magnetic hyperfine constant a' should vary as $\langle J_z\rangle$ which measures the electronic magnetization, and the quadrupole coupling constant P should vary as $\langle J_z^2-\frac{1}{3}J(J+1)\rangle$ which is a measure of the average value of the electronic quadrupole moment. Here, J corresponds to the ground state of the trivalent lanthanide ion. Below 239°K, terbium metal is ferromagnetic and thus in the liquid-helium range one can assume complete electronic magnetization, i.e., $\langle J_z\rangle$ can be replaced by $J=6$ and $\langle J_z^2-\frac{1}{3}J(J+1)\rangle$ by $J^2-\frac{1}{3}J(J+1)=22$. Therefore, a' and P may be treated as constants for present purposes.

Due to the magnetic hyperfine interaction, a nucleus with a spin I will have $2I+1$ possible spin orientations relative to H_{eff}. If the quadrupole interaction is assumed to be zero ($P=0$), the various nuclear energy levels are all equally spaced, the separation being $=a'$. If $P\neq 0$ the level scheme is changed; for terbium (the only stable isotope is Tb^{159} for which $I=3/2$), the energies W_i of the various nuclear spin states relative to the ground level W_0 become $W_1/k=a'-2P$, $W_2/k=2a'-2P$, $W_3/k=3a'$. At absolute zero only W_0 is populated; at 1°K the levels are already approximately equally occupied. Below 1°K, due to a redistribution among the spin orientations, a Schottky type anomaly is observed in the specific heat. The partition function for the nuclei can easily be written and the nuclear specific heat C_N calculated from it in the usual way. For terbium, one obtains[1]

$$\begin{aligned}C_N=(R/T^2)\{&(\tfrac{1}{2}a'^2+2P^2)\cosh(2a'/T)\\&+(2a'^2+2P^2)\cosh(a'/T)-2a'P\sinh(2a'/T)\\&-4a'P\sinh(a'/T)+\tfrac{1}{4}a'^2[9\exp(-2P/T)\\&+\exp(2P/T)]\}[\exp(-P/T)\cosh(3a'/2T)\\&+\exp(P/T)\cosh(a'/2T)]^{-2}. \qquad (2)\end{aligned}$$

Well above the maximum of the Schottky curve, one can write

$$C_N=DT^{-2}-ET^{-3}-FT^{-4}+GT^{-5}+HT^{-6}. \qquad (3)$$

The constants $D, \ldots, H$ are interdependent and may be expressed in terms of a' and P. If $P=0$ all the odd powers disappear.

Due to a spin-spin interaction between the $4f$ electrons of neighboring atoms, there is a magnetic specific heat C_M that can be observed for many rare earths even at liquid-helium temperatures. Well below the Curie point the simple spin wave theory[9] predicts for a ferromagnetic metal

$$C_M=cR(kT/2KS)^{3/2}=CT^{3/2}. \qquad (4)$$

Here, c is a constant depending on the number of nearest neighbors, K is the exchange integral, and S is the spin of the ground state of the lanthanide ion.

In addition to the nuclear and magnetic specific heats described above, there are the usual lattice and electronic contributions, $C_L=AT^3$ and $C_E=BT$, respectively. The specific heat of terbium metal can thus be written $C_p=C_L+C_E+C_M+C_N$; in analyzing the results, the observed C_p must be separated into these four components.

II. EXPERIMENTAL

The measurements were carried out in a He^3 cryostat which has been described earlier[10]; only a few of the most relevant experimental features are mentioned here. He^4 exchange gas was used to cool the sample down to 4.2°K. The space surrounding the calorimeter was then evacuated by pumping until a mass-spectrometer-type leak detector showed a very small helium reading. For further cooling, a mechanical heat switch was employed. This consists of a platform in thermal contact with the He^3 pot; the sample rests on the platform by its own weight and is thus cooled by contact. Since the nuclear specific heat of terbium is very large, it was necessary to use a little stopcock grease between the bottom of the calorimeter and the platform in order to reach the lowest temperatures (run II, cf. Table I) in a reasonable length of time. The grease contact was forcibly broken by lifting the sample when the measurements were begun. Due to the large heat capacity of the sample at this temperature, very little warming was observed when this was done. For this same reason and also because of the good thermal insulation, the temperature drift between heat inputs was hardly noticeable.

For the specific-heat measurements a colloidal graphite (Aquadag) thermometer was employed. It was calibrated after runs IA and IB against the vapor pressure of He^4 between 4.2 and 1.9°K, against the vapor pressure of He^3 between 1.9 and 0.75°K, and against a magnetic thermometer (chromium methylamine alum) between 0.75 and 0.37°K. For the short second experiment, calibration points were taken below 1.9°K only. He^4 temperatures were determined according to the T_{58} scale.[11] For He^3 the temperature scale of Sydoriak and Roberts[12] was used; corrections were made for the

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0.5% of He^4 in our He^3 gas and the temperatures[12] were changed to the T_{58} scale. The magnetic thermometer was calibrated against the vapor pressure of He^3. Forty calibration points for runs IA and IB and fourteen for run II were measured in this way.

The heat capacity of the empty calorimeter was known from an earlier experiment; it was always less than 1.5% of the heat capacity of the sample.

III. RESULTS

Our vacuum distilled terbium metal was prepared by Research Chemicals (Division of Nuclear Corporation of America) and analyses performed in our laboratory showed the following impurities: other metals not detected in spectrochemical analysis; hydrogen 0.02%, carbon 0.14%; nitrogen 0.01%; oxygen 0.12%. The sample, a cylinder 2.2 cm long and 2.7 cm in diameter, weighed 101.157 g (=0.63649 moles).

The experimental points are listed in Table I and are also plotted in Fig. 1. All calculations for these points were done on an IBM 704 digital computer[13]; these included the fitting of a seven-constant formula to the calibration points by the method of least squares, and the application of a curvature correction to the specific-heat data.

TABLE I. Specific heat (in mJ/mole °K) of terbium metal. Experimental results.

T(°K)	C_p	T(°K)	C_p	T(°K)	C_p
Run IA		Run IB		Run II	
0.4796	867.22	0.4681	904.03	0.3742	1299.09
0.5202	754.76	0.4872	843.76	0.3873	1217.57
0.5625	658.73	0.5077	786.27	0.4011	1151.81
0.6069	575.58	0.5297	730.23	0.4158	1087.07
0.6580	497.93	0.5534	676.79	0.4314	1023.48
0.7173	425.50	0.5791	626.80	0.4480	959.00
0.7873	358.86	0.6070	574.85	0.4658	893.28
0.8659	301.47	0.6373	526.76	0.4847	839.14
0.9492	254.79	0.6705	480.66	0.5050	780.76
1.0425	214.87	0.7069	436.81		
1.1454	181.88	0.7472	394.38		
1.2498	156.37	0.7918	354.79		
1.3620	135.55	0.8416	317.39		
1.4755	119.21	0.8974	282.24		
1.5780	107.83	0.9603	249.37		
1.6808	98.56	1.0318	218.88		
1.7927	90.70	1.1134	191.07		
1.9140	84.01	1.2071	165.76		
2.0441	78.41	1.3152	143.35		
2.1970	73.76	1.4402	123.72		
2.3723	70.24	1.5848	106.94		
2.5540	68.21	1.7511	93.31		
2.7391	67.60	1.9398	82.64		
2.9388	68.11	2.1498	75.07		
3.1645	70.01	2.3771	70.17		
3.4101	73.61	2.6154	67.82		
3.6685	79.03	2.8579	67.48		
3.9428	86.63	3.0973	69.20		
4.2322	96.50	3.3503	72.51		
		3.6120	77.36		
		3.8550	83.51		
		4.0787	90.40		

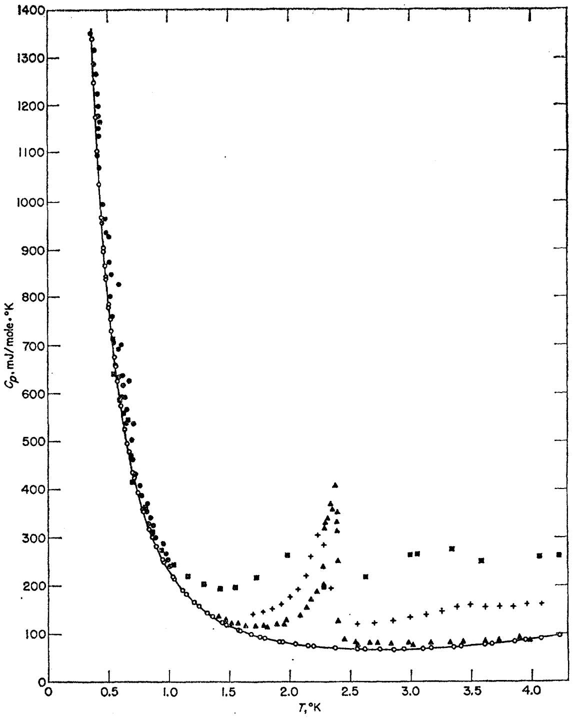

FIG. 1. The specific heat of terbium metal: ○, present results; □, Kurti and Safrata; (reference 3) ▲, Stanton, Jennings and Spedding; (reference 5) ●, Heltemes and Swenson; (reference 4) +, Bailey (reference 6). Solid curve $C_p=0.58T^3+9.05T+238T^{-2}-11.9T^{-3}-4.5T^{-4}+0.38T^{-5}+0.06T^{-6}$.

After a heating period the sample usually came to equilibrium in less than 10 sec. Only at the lowest temperatures were equilibrium times as long as 2 min encountered. This was not serious, however, since the heat leak to the sample produced almost no observable changes in temperature. The random scatter of the points (cf. Figs. 1 and 2) is only about 0.2%. Systematic errors in timing (by an electronic timer using a tuning fork frequency standard), heating current, heater resistance, and the heat capacity of the empty calorimeter total not more than 0.2% in the final results.

The main uncertainties in C_p are caused by the calibration of the carbon thermometer. The scatter of the calibration points was, with a few exceptions, less than 2 mdeg, and the He^4 and He^3 calibrations joined smoothly together. The calculated temperature is thus probably within 1 mdeg of the temperature defined by the He^4 and He^3 scales. Additional uncertainties of about 2 mdeg can arise from the extrapolation of the magnetic thermometer calibration below 0.75°K.

Considering all the above sources of error, but neglecting possible errors in the He^3 temperature scale, the accuracy of the present results is estimated as 0.8% between 1 and 4.2°K and 2% at 0.4°K. The systematic shift between the results from runs I and II (cf. Fig. 2)

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is caused by uncertainties in the thermometer calibrations.

The specific heat of terbium was separated into contributions by a least-squares analysis of all the experimental points. The results were: (C_p in mJ/mole °K) $C_L=0.58T^3$; $C_E=9.05T$; $C_N=238T^{-2}-11.9T^{-3}-4.5T^{-4}+0.38T^{-5}+0.06T^{-6}$. A preliminary calculation showed that the magnetic specific heat is small and in the final analysis C_M was assumed to be zero. The calculated curve fits the experimental data within 1.0%. The estimated accuracy of C_N is 2% and that of C_L and C_E is 5%.

Instead of expanding C_N in inverse powers of T [Eq. (3)], the exact expression of Eq. (2) can be used; our experimental results for the interaction parameters are: $a'=0.150$°K; $P=0.021$°K. In Fig. 2 the measured points below 2°K, after C_L and C_E have been subtracted, are plotted as C_NT^2 vs $1/T$. Calculated curves for the above values of a' and P and for $a'=0.150$°K, $P=0$ and for $a'=0.146$°K, $P=0$ are also shown. The results seem to indicate that a quadrupole term is necessary for explaining the experimental data on C_N. The polarization of the terbium nuclei within a given domain is 12% at 1°K and 29% at 0.4°K. Calculated values of C_N for terbium are listed in Table II; this shows that the maximum of the Schottky curve occurs at 0.08°K. The quadrupole coupling reduces the anomaly at the peak and shifts the maximum towards lower temperatures. To determine whether the entropy under the Schottky curve is R ln4, measurements would have to be extended down to 0.01°K.

TABLE II. C_N (in mJ/mole °K) of terbium metal calculated from Eq. (2) for $a'=0.15$°K, $P=0.021$°K.

T (°K)	C_N	T (°K)	C_N
0.01	20	0.50	799
0.02	1089	0.55	675
0.03	2898	0.60	577
0.04	4069	0.65	498
0.05	4681	0.70	434
0.06	4990	0.75	382
0.07	5132	0.80	339
0.08	5167	0.85	302
0.09	5127	0.90	271
0.10	5030	0.95	245
0.11	4890	1.00	222
0.12	4719	1.10	185
0.13	4529	1.20	156
0.14	4327	1.30	134
0.15	4120	1.40	116
0.16	3913	1.50	101
0.17	3710	1.60	89
0.18	3514	1.70	79
0.19	3325	1.80	71
0.20	3146	1.90	64
0.22	2816	2.00	58
0.24	2524	2.20	48
0.26	2268	2.40	40
0.28	2043	2.60	34
0.30	1847	2.80	30
0.32	1675	3.00	26
0.34	1525	3.20	23
0.36	1392	3.40	20
0.38	1275	3.60	18
0.40	1172	3.80	16
0.45	960	4.00	15
		4.20	13

IV. DISCUSSION

All the specific-heat measurements available at present for terbium below 4°K are shown in Fig. 1. Below 0.8°K, the data by Kurti and Safrata[3] agree very well with our results. Experiments by Heltemes and Swenson[4] below 1°K give systematically higher values of C_p but the agreement improves towards lower temperatures. They deduced $a'=0.15$°K from measurements above 0.4°K, in exact accord with our result, but, since P was assumed to be zero, the agreement is fortuitous.

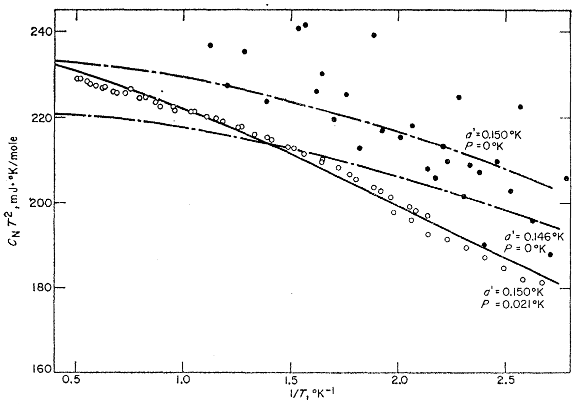

FIG. 2. Quadrupole interaction in the nuclear specific heat of terbium (see text). ○, present results; ●, Heltemes and Swenson (reference 4) (about 1/3 of points above 0.35°K are shown; the measurements extend down to 0.25°K).

Above 1°K, the present results follow a smooth curve and disagree sharply with earlier measurements, all of which show anomalies in C_p (cf. Fig. 1). The data by Stanton, Jennings, and Spedding[5] agree with our results at 1.4 and at 4°K but exhibit a pronounced λ-type anomaly centered around 2.4°K. A similar peak was found by Bailey,[6] but at a slightly lower temperature. His measurements and those of Kurti and Safrata[3] were made on the same piece of terbium metal, yet the results are quite different!

It seems probable that the anomalies are caused by impurities in the samples. That the impurity is Tb_2O_3 is suggested by Crane's[14] measurement of the heat capacity of a gadolinium sample in which the oxygen content was varied, and by recent measurements by Gerstein, Jelinek, and Spedding[15] on the magnetic susceptibility of Tb_2O_3; these measurements showed a maximum in the susceptibility, characteristic of antiferromagnetic ordering, at 2.42°K. Since the 0.12% oxygen content of our sample could have caused a

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rather large anomaly in the specific heat had magnetic ordering taken place in the liquid-helium range, the fact that no such effect was observed gives reason to believe that the oxygen of our sample is in a different form than in the sample of Stanton *et al.*[5]

A careful examination of both samples has been made by Bernard Beaudry who found the following: Each sample has two phases present—a major phase and a minor phase. In our sample the minor phase is more finely distributed than in Stanton's by about a factor of three. In addition, the minor phase in our sample appears to be precipitated along a crystallographic direction within each grain. Stanton's sample has the appearance of a eutectic surrounding terbium. Our sample has much more sharply defined grain boundaries than Stanton's. It is possible that the minor phase is Tb_2O_3.

The main difference between the two samples thus appears to be in the way the minor phase is distributed throughout the metal. More experiments are needed to determine why the anomaly did not show up in the heat capacity of our sample.

Our experimental result $C_L=0.58T^3$ corresponds to a Debye characteristic temperature $\theta=150$°K for terbium. This is in good agreement with the measurements of Jennings, Stanton, and Speeding[16] between 15 and 350°K which gave $\theta=158$°K.

Our value of 9.05 mJ/mole °K^2 for the coefficient B in the electronic specific heat of terbium can be compared with the experimental results $B=10.1$ for lanthanum,[17] 12.1 for samarium,[18] 9.5 for dysprosium,[10] 9.5 for lutetium,[19] 11.3 for scandium,[20] and 10.2 for yttrium[20] (the last two metals are not true rare earths but are frequently classed with them). C_E thus appears to be rather similar for these metals.

By putting $K=3.56k$,[21] $c=0.028$ (hcp lattice), and $S=3$ in Eq. (4), the spin-wave theory predicts $C_M=2.4$ mJ/mole °K$^{5/2}$. At 4°K, this would give a magnetic specific heat equal to about 50% of C_E. The experimental observation $C_M=0$, therefore, seems to indicate that this type of calculation using the exchange integral determined from the Curie temperature is not too accurate for terbium.[22]

Bleaney and Hill[1] have calculated the constants in Eqs. (2) and (3) from available electron paramagnetic resonance data on terbium ethyl sulfate, from nuclear magnetic resonance measurements on the metal, and from estimates based on Coulomb excitation. Their values are $D=250$ mJ °K/mole, $a'=0.152$°K, and $P=0.029$°K, all in good agreement with our calorimetric results. The approximate effective field at the terbium nucleus can be computed by writing $a'=\mu H_{\mathrm{eff}}/kI$ which, for $a'=0.150$°K and $\mu=1.52$ nuclear Bohr magnetons, gives $H_{\mathrm{eff}}=4.1$ MG, in good agreement with Kondo's[8] calculated result 4.2 MG. This work has been briefly published elsewhere.[23]

ACKNOWLEDGMENTS

We are very grateful to B. Beaudry for the metallographic examination of our sample and to Professor F. H. Spedding and Professor B. C. Gerstein (all of the Institute for Atomic Research, Ames, Iowa) for cooperation in this matter. We would also like to express our thanks to Dr. C. A. Bailey for permission to include his unpublished results in Fig. 1.

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[22] *Note added in proof.* Recent work on the magnetic specific heat of dysprosium by B. R. Cooper [Proc. Phys. Soc. (London) (to be published)] predicts an energy gap of the order of 20–30°K at the minimum of the spin wave spectrum. This gives an exponential temperature dependence for C_M at low temperatures, the value of C_M being quite small below 4°K. The theory seems applicable to terbium also and would explain why no magnetic specific heat was observed experimentally.

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