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Specific Heat of Holmium Metal between 0.38 and 4.2°K*

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Between 0.38 and 4.2°K, the specific heat of holmium metal can be expressed $C_p=2.26T^3+10T+C_N$ (in mJ/mole °K). For calculating the nuclear specific heat C_N a Schottky curve for eight energy levels at $W_i/k=a'i+P[i^2-\frac{1}{3}I(I+1)]$, where $i=-7/2,\cdots,7/2$, must be used. The magnetic hyperfine constant $a'=0.320$°K and the quadrupole coupling constant $P=0.007$°K. The results below 1°K indicate that a quadrupole term is necessary for representing the data with a Schottky curve. At 0.29°K, where the maximum is reached, $C_N=7000$ mJ/mole °K and even at 4°K $C_N=269$ mJ/mole °K, being thus larger than the other contributions to C_p combined. The effective magnetic field at the holmium nuclei is 9.3 MG. Owing to the very large hyperfine interaction the coefficient of the electronic specific heat was obtained from measurements on other rare earths. The T^3 term is the sum of lattice and magnetic specific heats and it was calculated from the present results above 2°K. The magnetic heat capacity apparently depends on the thermal history of the metal or on impurities.

I. INTRODUCTION

THE heat capacity of holmium metal has recently been measured between 0.95 and 14°K by Gordon, Dempesy, and Soller[1] and between 1.4 and 4°K by Dreyfus, Goodman, Lacaze, and Trolliet.[2] The results revealed a huge nuclear contribution (C_N) to the specific heat of this rare earth, in fact, even at 4°K C_N is larger than the lattice (C_L), electronic (C_E), and magnetic (C_M) specific heats combined. C_N was expressed by a Schottky-type equation for eight equally spaced levels.

We have measured the specific heat of holmium between 0.38 and 4.2°K. The experiments were undertaken for two reasons: First, by extending the measurements well below 1°K, possible deviations from the Schottky curve based on equally spaced levels might be detected. Such changes in the energy level scheme could be caused by nuclear electric quadrupole coupling.[3] Second, in view of the fact that the two measurements[1,2] on holmium mentioned above disagree by about 10% between 3 and 4°K and that for many rare earths[4] considerable discrepancies have been observed between the results of different investigators especially above 1°K, it was thought advisable to extend our measurements up to 4.2°K.

The nuclei in many rare-earth metals find themselves in a strong effective magnetic field H_{eff} (Marshall,[5] Kondo[6]) which arises from several sources: (1) The magnetic momenta of other rare-earth ions produce a field of about 10 to 20 kG. (2) Polarization of the conduction electrons by the 4*f* electrons will cause an effective field which, from measurements on hyperfine interaction in the 3*d* metals, can be estimated as 200 to 400 kG. (3) The orbital angular momenta of the 4*f* electrons produce a large field at the nucleus of the same atom. This field is of several megagauss. (4) The spin angular momenta of the 4*f* electrons also cause an effective field at the nucleus. This field is about one tenth of that caused by the orbital angular momenta. (5) Polarization of the inner shell electrons by the spins of the 4*f* electrons may also produce an effective field at the nucleus. The magnitude of this field can be estimated from electron spin resonance experiments on Gd^{3+} and Eu^{++} ions in which the 4*f* shell is half full and, consequently, the orbital angular momentum is zero. The estimates are about 300 kG. The main contribution to H_{eff} thus comes from the orbital angular momenta of the 4*f* electrons.

In addition to H_{eff}, 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. Bleaney and Hill[3] and Bleaney[7] write the Hamiltonian for the nuclei in the form

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

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 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 19°K holmium metal is ferromagnetic and one can thus assume complete electronic magnetization a few degrees above the absolute zero, i.e., $\langle J_z\rangle$ can be replaced by $J=8$ and $\langle J_z^2-\frac{1}{3}J(J+1)\rangle$ by $J^2-\frac{1}{3}J(J+1)=40$. a' and P are thus treated as temperature-independent constants.

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[5] W. Marshall, Phys. Rev. **110**, 1280 (1958).

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Due to the hyperfine interaction the holmium nucleus with a spin $I=7/2$ (the only stable isotope of holmium is Ho^{165}) will have, relative to H_{eff}, eight possible spin orientations. The energies W_i of the various nuclear spin states, i.e., the eigenvalues of the Hamiltonian in (1), are

$$W_i/k=a'i+P[i^2-\tfrac{1}{3}I(I+1)], \qquad (2)$$

where $i=-I, -I+1, \cdots, I$. If no quadrupole interaction is assumed ($P=0$), the energy levels are equally spaced, their separation being $=a'$; if $P\neq 0$ the level scheme is changed. At 0°K only the lowest level is occupied, but as the temperature is increased the higher levels will gradually become populated. This is readily observed as a Schottky-type anomaly in the heat capacity. By writing the partition function this nuclear specific heat can be calculated in the usual way. The general exact formula becomes

$$C_N=\Big[R\sum_{i=-I}^{I}\sum_{j=-I}^{I}(W_i^2-W_iW_j)\exp(-W_i-W_j)/kT\Big]\Big/\Big[(kT)^2\sum_{i=-I}^{I}\sum_{j=-I}^{I}\exp(-W_i-W_j)/kT\Big]. \qquad (3)$$

For most rare earths, Eq. (3) can be expanded above 0.4°K in inverse powers of T, the leading term being proportional to T^{-2}. In the case of holmium, however, the hyperfine interaction is so strong that the exact expression (3) must be used.

In addition to the nuclear specific heat discussed above and the usual lattice and electronic contributions, $C_L=AT^3$ and $C_E=BT$, respectively, a magnetic specific heat, due to spin-spin interactions between the $4f$ electrons of neighboring atoms, can be observed for many rare earths even at liquid helium temperatures. Sufficiently far below the Curie point the magnetic specific heat may be calculated approximately by means of the spin wave theory, which, for a simple ferromagnetic metal, predicts $C_M\propto T^{3/2}$.

The magnetic structure of holmium has been determined by Koehler[8] using neutron diffraction techniques. At low temperatures, the $4f$ electronic spins all lie on the surface of a cone, the axis of which is parallel to the c axis of the hcp lattice (this is also the direction of propagation of the spin waves). The transverse components of the spin vectors along the c axis form a simple spiral; the much smaller longitudinal components are constant. Kaplan[9] has obtained the interesting result that, for such a ferromagnetic spiral, $\omega(\mathbf{k})$ is linear in $\mathbf{k}$ for small values of the wave vector, even though the net spin is not zero. The reason for this linear dispersion law, similar to that deduced in the antiferromagnetic case, was attributed to the fact that the normal modes correspond approximately to oscillations of the components perpendicular to the magnetization, these components themselves forming an antiferromagnetic structure. From this one can conclude that for holmium at low temperatures $C_M\propto T^3$, the temperature dependence of the magnetic specific heat being the same as for an antiferromagnetic substance.

By analyzing their results between 4 and 14°K, Gordon *et al.*[1] concluded that $C_M\propto T^n$, where $2<n<3$. We have re-examined their data and find $n=3$ between 4 and 8°K; the value of n decreases towards higher temperatures due to the proximity of the Curie point at 19°K. In view of this experimental evidence and Kaplan's[9] calculations, we have assumed $C_M\propto T^3$ in analyzing our results. The specific heat of holmium may thus be written $C_p=AT^3+BT+C_N$, where the first term is the sum of C_L and C_M, and C_N is given by Eq. (3).

II. EXPERIMENTAL

The heat capacity measurements were carried out in an He^3 cryostat which has been described earlier by Lounasmaa and Guenther[4]; only the most important experimental features are related here. After cooling the sample down to 4.2°K by He^4 exchange gas, the space surrounding the calorimeter was 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 reservoir, on which the sample rests by its own weight and is cooled by contact. Since the nuclear specific heat of holmium is very large, it was necessary, for reaching the lowest temperatures in a reasonable length of time, to use a little stopcock grease between the bottom of the calorimeter and the platform. 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 0.4°K very little warming was observed when this was done. In order to repeat the measurements the sample had first to be warmed up to room temperature so that an effective grease contact could again be made.

For the specific heat measurements a colloidal graphite (Aquadag) thermometer was employed. It was calibrated after both experiments, before the cryostat was warmed up above 4.2°K, 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 0.38°K. He^4 temperatures were determined according to the T_{58} scale.[10] For He^3 the temperature scale of Sydoriak and Roberts[11] was used; corrections were made for the 0.5% of He^4 in our He^3

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gas and the temperatures[11] were changed to the T_{58} scale. The magnetic thermometer was calibrated against the vapor pressure of He^3.

The heat capacity of the empty calorimeter, measured in a separate experiment, was always less than 1% of the heat capacity of the holmium sample.

III. RESULTS AND DISCUSSION

Our holmium metal was purchased from Research Chemicals, Inc. (Division of Nuclear Corporation of America). It was vacuum distilled, then remelted in a vacuum and cast into a tantalum crucible. Next, the tantalum was machined off and the sample turned down to a cylinder 0.8 cm long and 2.8 cm in diam; its weight was 41.390 g (=0.25094 mole). The following impurities were detected in our laboratory: other metals not found in spectrochemical analysis, hydrogen 0.005%, carbon 0.07%, nitrogen 0.07%, oxygen 0.21% (by weight).

Two completely independent runs were made on our sample. The experimental results are listed in Table I and the points are also plotted in Fig. 1. All calculations were done on an IBM 704 digital computer.[12] The results have been corrected for curvature.

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

T (°K)	C_p	T (°K)	C_p
Run I		Run II	
0.3817	6577	0.4471	6252
0.4066	6447	0.4735	6183
0.4345	6331	0.5032	6043
0.4662	6210	0.5361	5882
0.4985	6039	0.5702	5699
0.5311	5877	0.6054	5478
0.5654	5606	0.6422	5227
0.6008	5398	0.6808	4968
0.6375	5204	0.7218	4681
0.6753	5129	0.7652	4393
0.7152	4665	0.8117	4092
0.7583	4417	0.8617	3794
0.8040	4151	0.9159	3493
0.8529	3861	0.9746	3218
0.9057	3576	1.0389	2922
0.9625	3291	1.1107	2627
1.0246	3015	1.1901	2354
1.0939	2706	1.2788	2100
1.1705	2418	1.3787	1855
1.2558	2166	1.4921	1628
1.3515	1923	1.6217	1421
1.4599	1697	1.7713	1226
1.5809	1481	1.9369	1057
1.7230	1282	2.1117	915
1.8876	1103	2.2925	806
2.0796	941	2.4878	709
2.3047	799	2.7089	628
2.5697	679	2.9559	566
2.8795	583	3.2287	515
3.2344	514	3.5246	480
3.6295	468	3.8353	460
4.0497	453	4.1533	459

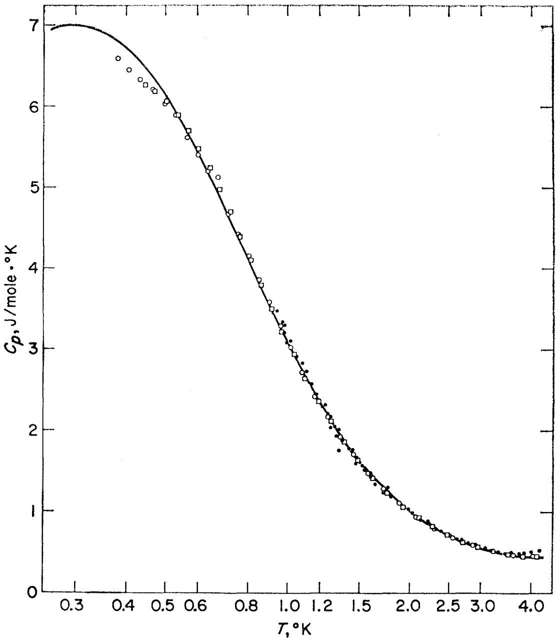

FIG. 1. The specific heat of holmium metal: ○, run I; □, run II; solid curve, $C_p=2.26T^3+10T+C_N$ (C_N given in Table II); ●, Gordon, Dempesy, and Soller.[1]

After a heating period the sample usually came to equilibrium in less than ten seconds. Only at the lowest temperatures were equilibrium times as long as 2 to 4 min observed. This was not serious, however, since the heat leak to the sample was so small in relation to its heat capacity that the temperature drift was hardly noticeable. The random scatter of the points within each run, with a few isolated exceptions, 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 random scatter of the calibration points was about 1 mdeg or less, and the He^4 and He^3 calibrations joined smoothly together. However, at the lowest temperatures, because of the very large heat capacity of the holmium sample, 30 to 40 min were required to bring the magnetic and carbon thermometers into equilibrium. Small systematic errors are thus possible below 0.6°K. Additional uncertainties of about 2 mdeg may arise from the extrapolation of the magnetic thermometer calibration below 0.75°K. Considering all the above sources of error the accuracy of the present results is estimated as 0.8% between 1 and 4.2°K, 2% at 0.6°K, and 3% at 0.4°K.

The nuclear specific heat of holmium is so large that for determining the interaction parameters a' and P in Eq. (2), C_L, C_E, and C_M may be neglected below 1°K,

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[12] P. R. Roach, Argonne National Laboratory Technical Report No. 6497, 1962 (unpublished).

and very crude estimates are sufficient up to 2°K. The Schottky curve (3) was computed for many different values of these parameters; the best fit with experimental results below 2°K was obtained for $a'=0.320$°K $\pm3\%$, $P=0.007$°K$\pm20\%$. Owing to predominance of C_N the other contributions to C_p can be determined only with fair accuracy. By assuming, in accordance with measurements[4] on other rare earths, $C_E=10T$ (mJ/mole °K), the result $C_L+C_M=2.26T^3$ was deduced from our data above 2°K. If we further assume that the lattice specific heats of holmium and terbium are equal, we obtain, by using data by Lounasmaa and Roach,[4] $C_L=0.58T^3$ and $C_M=1.68T^3$.

The calculated curve $C_p=2.26T^3+10T+C_N$ (in mJ/mole °K), C_N being listed in Table II, is shown in Fig. 1. The fit to the experimental points is reasonably good. The maximum in C_p occurs at 0.29°K and the minimum approximately at 4.2°K. For determining whether the entropy associated with C_N is $R\ln 8$, measurements would have to be extended down to 0.03°K. At 1°K the polarization of the holmium nuclei within a domain is 42% and at 0.4°K it is 75%. Owing to its very high heat capacity, holmium could be used as a convenient constant temperature bath at 0.3°K.

Most of the specific heat points by Gordon, Dempesy, and Soller[1] below 4.2°K are plotted in Fig. 1 for comparison. The agreement is very satisfactory except near 4°K where our results are somewhat lower. Measurements by Dreyfus, Goodman, Lacaze, and Trolliet[2] have been published only in the form of a smoothed equation $C_p=1.3T^3+26T+C_N$ ($a'=0.302$°K, $P=0$, C_p in mJ/mole °K). Even though their expression for C_p has rather different coefficients from ours, their total C_p is only a few percent lower than ours in the overlapping region between 1.4 and 4°K.

TABLE II. C_N (in mJ/mole °K) of holmium metal calculated from Eq. (3) for $a'=0.320$°K, $P=0.007$°K.

T (°K)	C_N	T (°K)	C_N
0.01	0	0.55	5800
0.02	2	0.60	5439
0.03	68	0.65	5081
0.04	385	0.70	4735
0.05	994	0.75	4406
0.06	1758	0.80	4097
0.07	2540	0.85	3811
0.08	3260	0.90	3545
0.09	3888	0.95	3301
0.10	4420	1.00	3077
0.11	4864	1.10	2683
0.12	5235	1.20	2353
0.13	5542	1.30	2075
0.14	5798	1.40	1839
0.15	6011	1.50	1640
0.16	6190	1.60	1470
0.17	6340	1.70	1323
0.18	6466	1.80	1197
0.19	6573	1.90	1087
0.20	6662	2.00	992
0.22	6801	2.20	834
0.24	6897	2.40	710
0.26	6958	2.60	612
0.28	6991	2.80	532
0.30	6998	3.00	467
0.32	6983	3.20	413
0.34	6947	3.40	368
0.36	6893	3.60	329
0.38	6822	3.80	297
0.40	6737	4.00	269
0.45	6470	4.20	244
0.50	6150		

The present measurements have shown that in order to represent the nuclear specific heat of holmium below 1°K by a Schottky curve a quadrupole term in Eq. (2) is necessary. If our data above 1°K only are considered, a good fit can be obtained for $a'=0.306$°K, $P=0$, instead of $a'=0.320$°K, $P=0.007$°K. The former result is in good agreement with Gordon *et al.*[1] ($a'=0.309$°K, $P=0$) and Dreyfus *et al.*[2]

Bleaney[7] has calculated the constants in Eq. (2) from available electron paramagnetic resonance data. His values for holmium are $a'=0.311$°K, $P=0.001$°K. The quadrupole coupling constant is considerably smaller than that deduced from our specific heat results.[13] The effective magnetic field at the holmium nuclei can be computed approximately by writing $a'=\mu H_{\text{eff}}/kI$ which, for $a'=0.320$°K and $\mu=3.3$ nuclear Bohr magnetons, gives $H_{\text{eff}}=9.3$ MG, in good agreement with Kondo's[6] calculated result 9.0 MG.

Experimental values available at this time for the coefficient of the T^3 term in C_p are (in mJ/mole °K^4): 2.26 (present results), 1.3 (Dreyfus *et al.*[2]), 3.3 (calculated by us from the data of Gordon *et al.*[1] between 4 and 8°K). The different results are most probably caused by differences in the magnetic specific heat. C_M might depend on the speed with which the sample was cooled over the transition region[14] (a result suggesting this was obtained by Lounasmaa[4] for samarium), on the earlier thermal history of the metal, or on impurities. It should perhaps be mentioned here that during an early preliminary experiment we obtained for holmium near 4°K a considerably higher specific heat than that presented in this paper. The result could, at least partly, be real, but considerable difficulties in thermometry prevailing during that experiment might also be responsible for it. In order to clarify the situation, specific heat and magnetic measurements should be made on holmium between 2 and 25°K.

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The author is indebted to Professor J. E. Gordon for making his results above 4°K available prior to publication and to B. D. Holt and J. P. Faris for analyses of the holmium sample.

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[13] *Note added in proof.* On the basis of recent atomic beam experiments on holmium by L. S. Goodman, H. Kopfermann, and K. Schlüpmann (reported at the VI Brookhaven Conference on Molecular Beams, June 1962), a new calculation by Bleaney (private communication) gave $P=0.003$°K. Transmission experiments with polarized neutrons by H. Postma, H. Marshak, V. L. Sailor, F. J. Shore, and C. A. Reynolds [Phys. Rev. **126**, 979 (1962)], gave $a'=0.32_5\pm0.04$°K in good agreement with our calorimetric value.

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