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Calorimetric Investigation of Hyperfine Interactions in Metallic Ho and Tb†

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The specific heats of metallic Ho and Tb have been measured between 0.03 and 0.5°K, a temperature range in which the nuclear (hyperfine) heat capacity predominates. The data are fitted with theoretical Schottky curves, using magnetic dipole hyperfine-interaction parameters $a' = +0.319$°K and $a' = +0.149$°K, and electric quadrupole coupling constants $P = +0.004$°K and $P = +0.0158$°K for Ho and Tb, respectively. For Tb, these values are in agreement with the parameters obtained from nuclear-magnetic-resonance measurements. An earlier suggestion by the present authors that a cooperative nuclear-magnetic-nuclear interaction might be present in Tb is here shown to have been based on an erroneous temperature scale. A detailed description of the calorimeter is presented.

I. INTRODUCTION

HYPERFINE interactions in the rare-earth elements have been the subject of considerable theoretical and experimental interest in recent years.[1–3] Experimentally, it has been shown that the hyperfine interaction constants for the rare earths are nearly the same irrespective of whether the nucleus is located in a metal or in a salt. This has been explained theoretically by the fact that for most of the rare earths the hyperfine fields originate predominantly from the electrons in the unfilled $4f$ shell of the host ion, and that these $4f$ electrons in turn occupy a rather well-protected environment within the electron cloud of that ion. As a result, the effects due to neighboring ions and nuclei, conduction electrons, or electrons other than $4f$ in the host ion, only perturb the fields established by the $4f$ electrons. For technical reasons, which will be explained below, few quantitative data have been obtained concerning these interactions in many of the rare-earth metals. It is the purpose of the present work to provide such data.

If a nucleus has spin I and magnetic moment μ, it may occupy any one of the $(2I+1)$ Zeeman energy levels $W_m(m=I,\cdots,-I)$ which are produced by the interaction of μ with a magnetic field H at the site of the nucleus. A knowledge of the spacing of the energy levels therefore provides information concerning the hyperfine fields within the material. A direct determination of the spacing or splitting of the levels W_m in a rare-earth metal may be obtained from Mössbauer or NMR experiments. Information is also available from neutron-transmission measurements of the nuclear magnetic susceptibility, but this requires a prior knowledge concerning the interaction Hamiltonian since the level spacing is lost within a sum over all levels. The same is true for specific-heat measurements. The heat capacity C_N arising from a discrete set of hyperfine energy levels W_m is a Schottky anomaly with a peak or maximum at a temperature $T \approx \langle \Delta W \rangle_{\mathrm{av}}/k$, where $\langle \Delta W \rangle_{\mathrm{av}}$ is the mean spacing of the energy levels and k is the Boltzmann constant.

Fortunately the leading terms in the interaction Hamiltonian $\mathcal{H}$ are known, since they are due to nuclear interactions with the $4f$ electrons. In addition, the fields will be the same at all nuclei since at the temperatures of interest here the electronic system is completely polarized. Then, if there is a nuclear electric quadrupole moment eQ' in addition to μ,

$$\mathcal{H} = (\mu H/I)I_z + [3e^2qQ'/4I(2I-1)] \times [I_z^2 - \tfrac{1}{3}I(I+1)], \quad (1)$$

where eq is the electric-field gradient at the nucleus.[1] It is assumed that H and eq are parallel and define the z axis, and that they include contributions from the core and conduction electrons.[4] The eigenvalues of Eq. (1) are

$$W_m/k = a' + P[m^2 - \tfrac{1}{3}I(I+1)]. \quad (2)$$

The equally spaced Zeeman energy levels are therefore systematically shifted relative to each other by the quadrupole interaction. A smaller shifting which would be caused by off-diagonal components in the quadrupole term of Eq. (1) has been ignored as being too small to be resolved in the present experiments.

Analysis of a heat-capacity (or neutron-transmission) measurement now becomes tractable since only two parameters, a' and P, need to be extracted. Nevertheless, it is obvious that Mössbauer and NMR measurements give a more precise picture of the level splittings. Unfortunately, the first method is often limited by a lack of suitable nuclei, and the latter by difficulties in producing NMR in metallic samples. Since heat-capacity techniques are applicable to any sample, much of our knowledge concerning the magnitude of the hyperfine parameters in rare-earth metals has come from heat-capacity measurements. In addition, calorimetric measurements made at very low temperatures deter-

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[1] *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967).

[2] R. L. Mössbauer, Rev. Mod. Phys. 36, 362 (1964).

[3] See the Proceedings of Sixth Rare-Earth Conference, Gatlinburg, 1967 (unpublished).

[4] B. Bleaney, J. Appl. Phys. 34, 1024 (1963).

mine the sign of P as well as indicate any anamolous behavior, such as cooperative effects, that may be present.

The interaction constant a' is of order 0.1°K, and so the Schottky anomaly is centered near this temperature in a plot of the specific heat versus temperature. Below roughly 0.3°K the nuclear contribution C_N represents 99% or more of the total heat capacity of the sample since contributions from conduction electrons, phonons, and magnetic excitations decrease with decreasing temperature. Most heat-capacity measurements, however, have only extended down to $\approx 0.4°K$, which includes, for most of the rare-earth metals, only the high-temperature tail of the Schottky curve—and this somewhat obscurely because of uncertainties in the other contributions to the heat capacity. We therefore undertook a series of measurements of the heat capacities of rare-earth metals in the temperature range 0.02–0.5°K in order to make detailed comparisons both with theory and with the results of other techniques.

The first samples were chosen to be Ho and Tb, primarily because the heat capacity of these metals had been measured down to 0.06°K by van Kempen *et al.*,[5] and we hoped thereby to be able to check the operation of our calorimeter. The results of our measurements are presented in Sec. III and are compared with theoretical calculations and the results of other experiments.

II. EXPERIMENTAL

The standard technique was employed whereby a measured amount of heat Q was introduced to the sample, the resulting change in temperature ΔT noted, and the heat capacity C computed from $Q/\Delta T$. Hence in the following description the emphasis will be on temperature calibration and thermal equilibrium.

The calorimeter, shown in Fig. 1, consisted of an epoxy frame[6] on which the various parts were mounted and which was supported from the top by a thin-wall nylon tube. The upper end of the tube contained a threaded copper piece which screwed onto the bottom of an adiabatic demagnetization refrigerator. A copper wire was indium-soldered[7] to the copper piece and to one end of a tin thermal switch ($A/l = 2.6 \times 10^{-3}$ cm) which was activated by a small Nb-Zr superconducting coil. Another copper wire was indium-soldered to the lower end of the switch, to a resistance thermometer (R_T), and to a threaded copper post. At the bottom end of the epoxy frame, a roughly spherical arrangement of 3.99 g of thin cerium magnesium nitrate (CMN) single crystals was thermally attached with Apiezon N grease to copper coil-foils.[8] The foils were indium-soldered to a copper wire and a second resistance thermometer (R_B). All of the foregoing remained undisturbed in the cryostat during all of the measurements.

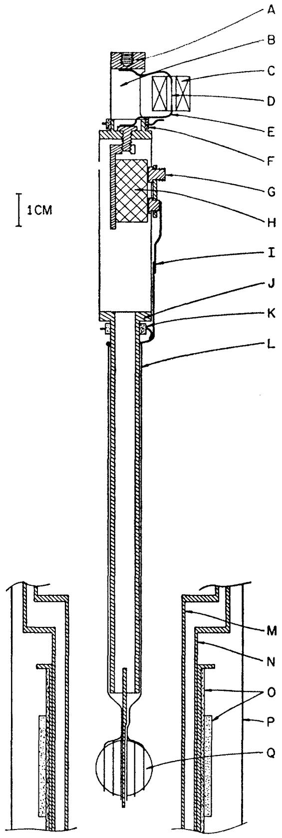

FIG. 1. Calorimeter construction. A—high purity copper, B—thin-wall nylon tube, C—coil for tin thermal switch D, E—annealed copper wires, F and K—resistance thermometers, G—heater, H—sample, I—indium solder joint, J—epoxy frame, L—coil-foil, M—0.02°K shield, N—0.3°K shield and vacuum jacket, O—mutual inductance coils, P—4°K vacuum jacket, Q—magnetic thermometer.

Each metallic rare-earth sample was mounted on an L-shaped piece of high-purity copper which had a threaded hole at one end. Two copper buttons were mounted on the opposite, free surface of the sample as shown in Fig. 1. An electrical heater with superconducting leads was attached to one button, a copper wire to the second. Thermal contact was obtained between the sample, the two copper buttons, and the L-shaped piece by scraping away the oxide layers on all mating surfaces while they were covered with a thin coating of liquid In-Hg solution.[9] The pieces were then held together with nylon thread as shown in Fig. 1. It is believed that the superconducting In-Hg layer did not of itself provide the excellent thermal contact achieved, but rather served to keep the surfaces clean so that electronic thermal contact was provided between the mated pieces.[7] After the sample had been mounted, the assembly was screwed onto the threaded post in the calorimeter and the two copper wires indium-soldered together.

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

[6] Epibond 100a, sold by Furane Plastics, 4516 Brazil Street, Los Angeles, California.

[7] M. Suomi, A. C. Anderson, and B. Holmström, Physica **38**, 67 (1968).

[8] Coil-foil or wire-foil is a sheet of insulated copper wires (bonded together with varnish) which provides thermal transport without being susceptible to eddy-current heating.

[9] This mixture was rather arbitrarily concocted of roughly 43% In, 53% Hg, and 4% Bi by mass. The mixture could be removed easily from the surface of the sample with a tissue. See V. J. King, Rev. Sci. Instr. **32**, 1407 (1961) for a more complete description of such alloys.

Thermal shields at 0.02 and 0.3°K were then put in place, and finally a stainless steel (# 304) vacuum jacket at 4°K.

The resistance thermometers were 220-Ω, 0.5-W Speer carbon resistors.[10] These were wrapped with coil-foil and indium-soldered directly onto the calorimeter in order to improve thermal contact and decrease their thermal response time. Resistances were measured with an ac Wheatstone bridge using synchronous detection. The heater power was determined by measuring current and voltage using a digital voltmeter, and the heating interval was measured by a digital timer. The mutual inductance of the magnetic thermometer was measured using a device, similar to that described by Maxwell,[11] employing synchronous detection. The mutual inductance coils, similar in geometry to those described by Abel *et al.*,[12] were mounted on the 0.3°K thermal shield and hence were wound with a superconducting primary. By placing a few turns of wire near one end of the coil and passing through it a known fraction of the 17 cps primary current we could ascertain that the entire system was linear to better than 1:10^4 over its complete range. A run without CMN present showed no detectable temperature-dependent magnetic background. The rms measuring field was about 0.5 G.

The CMN was calibrated against the vapor pressure of He^3 in the temperature range 0.8–2°K.[13] The main pumping tube of the He^3 refrigerator was used as a sensing probe, to avoid thermomolecular corrections,[14] while the temperature was maintained by pumping through a small auxiliary tube. During calibration the 4°K jacket was evacuated while the jacket attached to the He^3 refrigerator contained He^3 thermal exchange gas. The temperature of the latter jacket was maintained constant to 1:10^5 during a vapor-pressure measurement by using an electronic regulator and an electrical heater, although the heating rate was never large enough to cause a detectable temperature rise due to the Kapitza resistance of the liquid He^3. The vapor pressure was measured in a wide-bore Hg manometer taking great care in the illumination of the meniscus and correcting for gravity and the temperature of the Hg. The He^3 was purified of He^4 so no impurity correction was necessary.[15,16] The resulting calibrations are accurate to roughly $\pm 0.2\% \pm 10^{-4}$ °K.[17] Calibrations made prior to and following an experimental run always agreed within the stated accuracy. Calibrations after cycling the cryostat to room temperature and changing samples were always the same to ±1%.

The constant uncertainty of $\pm 10^{-4}$ °K in the calibration is due to the shape correction (demagnetizing factor) of the CMN. The net shape correction of this thermometer was measured relative to a sphere of CMN by placing the sphere and the thermometer in opposing arms of a mutual inductance bridge and observing the bridge unbalance as a function of temperature.[18] If T is the thermodynamic temperature and T^* is the "magnetic" temperature related to the susceptibility of the CMN, the correction Δ enters as $T = T^* + \Delta$. The Δ measured for our thermometer was $(2.8 \pm 0.1) \times 10^{-3}$ °K. The size of this correction is startling. It is of a magnitude normally expected of a thin single crystal of CMN similar to the individual crystals which were used in the thermometer. An earlier estimate of Δ based on the *external* shape of the CMN package[19] and the divergent magnetic field gave $0 < \Delta < 0.001$°K. The resulting erroneous temperature scale led the present authors to suggest that an effective-nuclear interaction might be present in Tb metal.[20] As discussed in Sec. III, the data may now be analyzed without need of such an interaction.

Extrapolation of the CMN calibration below 0.8°K assumes a Curie-law behavior. Such behavior has been verified to within ±1% down to 0.006°K,[21] and recent investigations suggest that it is even better than this.[22,23] As a check on the magnetic thermometer the resistance thermometers had previously been calibrated down to 0.03°K against a similar thermometer using CMN obtained and grown separately from the CMN used in the calorimeter. The calibration of the resistance thermometers remained constant for at least a year, and agreed with the calibration of the CMN in the calorimeter to within their accuracy of roughly ±1%.

A typical heat-capacity measurement is shown in Fig. 2. A temperature drift is established using the magnetic thermometer. Q is added, and the temperature drift is again established. The drifts were then extrapolated graphically to a time t_m and the change ΔT computed. The time t_m was determined from a plot of R_T versus time, since this thermometer gave an accurate determination of the heat exchanged with the outside (via the tin thermal switch) during the transient period

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[10] W. C. Black, Jr., W. R. Roach, and J. C. Wheatley, Rev. Sci. Instr. **35**, 587 (1964).

[11] E. Maxwell, Rev. Sci. Instr. **36**, 553 (1965).

[12] W. R. Abel, A. C. Anderson, and J. C. Wheatley, Rev. Sci. Instr. **35**, 444 (1964).

[13] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. (U. S.) **68A**, 579 (1964).

[14] G. T. McConville, R. A. Watkins, and W. L. Taylor, Ann. Acad. Sci. Fennicae **A VI210**, 44 (1966).

[15] T. R. Roberts, R. H. Sherman, S. G. Sydoriak, and F. G. Brickwedde, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1964) Vol. IV, p. 480.

[16] A. C. Anderson, Cryogenics **8**, 50 (1968).

[17] The ±0.2% does not allow for any deviation of the T_{62} scale from a thermodynamic-temperature scale. A deviation of order 0.3% is becoming apparent; see H. Plumb and G. Cataland, Metrologia **1**, 127 (1966); and J. S. Rogers, R. J. Tanish, M. S. Anderson, and C. A. Swenson, *ibid.* (to be published).

[18] A. C. Anderson, J. Appl. Phys. (to be published).

[19] J. A. Osborn, Phys. Rev. **67**, 351 (1945).

[20] A. C. Anderson, B. Holmström, and M. Krusius, Phys. Rev. **20** 154 (1968).

[21] J. M. Daniels and F. N. H. Robinson, Phil. Mag. **44**, 630 (1953).

[22] R. B. Frankel, D. A. Shirley, and N. J. Stone, Phys. Rev. **140**, A1020 (1965); **143**, 334 (1966).

[23] R. P. Hudson and R. S. Kaeser, Physics **3**, 95 (1967).

and hence permitted application of the "equal-areas" rule.[24] The midpoint of the heating period differed from t_m only at the lowest temperatures where the thermal diffusivity of the samples was small. Even then this difference would have caused $<1\%$ error in the computation of C.

The error caused by heat leak or temperature drift could be checked as follows. The thermal time constant of the sample could be measured at the lowest temperatures, thus allowing an estimate to be made of the thermal conductivity K since the heat capacity was also measured. K was found to be linear in temperature and of magnitude similar to that measured at higher temperatures.[25,26] From K and the measured heat leak the temperature differential across the sample was computed and found to be too small to require correction in the computation of C. This was substantiated by measuring C using the two resistance thermometers on *opposite* sides of the sample. They indicated the same ΔT to within $\pm 2\%$, which also agreed with the ΔT as measured by the magnetic thermometer. This was true irrespective of the sign or magnitude of the heat leak, which could be varied since over most of the temperature range the heat leak was via the tin thermal switch and was influenced by the current in the switch coil and the temperature of the demagnetization refrigerator. The foregoing serves to prove that the thermal time constant within the calorimeter was much shorter than the time constant of the calorimeter relative to its environment.

The residual heat leak to the calorimeter, that is, the heat leak at the lowest temperatures where the heat flux from the calorimeter through the tin thermal switch was essentially zero, was 0.3–2 erg/min. This was partially due to vibration and partially due to very low level rf radiation from the electronics. The cryostat and all measuring apparatus were enclosed in a shielded room because of the proximity of radio transmitters.

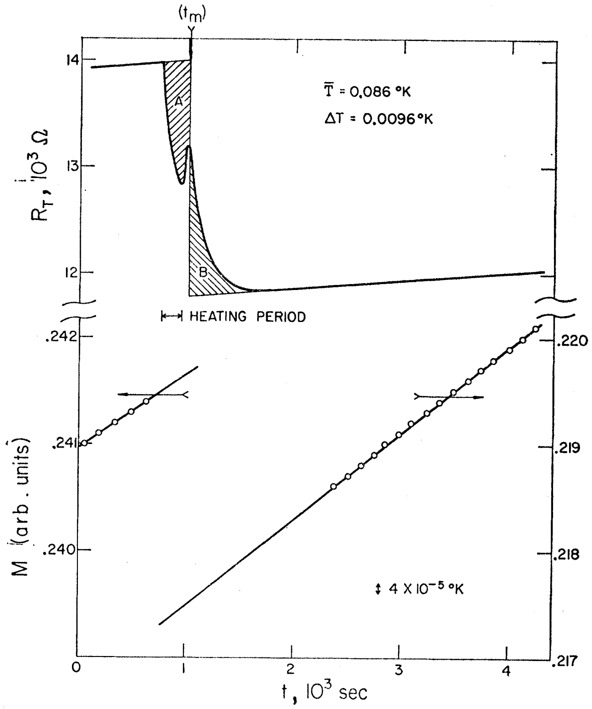

FIG. 2. Readings of the upper-resistance thermometer R_T and the magnetic thermometer M, versus time t. The heating period is indicated. Setting area A = area B determines the time t_m to which M is extrapolated. Using the midpoint of the heating period rather than t_m would introduce an error of $\approx 0.1\%$. The details of R_T versus t vary with sample and temperature. Note that the relative shift in scale for the two M curves is greater than the height of this page. The heat leak for the above data was ~20 erg/min out of the calorimeter. This was reduced later in the run by a better adjustment of the current in the thermal switch coil.

The heat capacity of the calorimeter was estimated from the amounts of various materials present. Above 0.1°K the heat capacity of the empty calorimeter was also measured. Here the thermal isolation of the calorimeter was increased by substituting a Sn thermal switch with 10^{-2} the area-to-length ratio normally used. The estimate and the measurement agreed within 12% at 0.5°K. The ratio of the calorimeter heat capacity to the Tb heat capacity at 0.55°K was 3.8×10^{-3}. A more serious problem occurs for Ho at low temperatures, since C_N is then rather small. The estimated heat capacity of the calorimeter at 0.04°K is large due to the magnetic heat capacities of CMN[23] and manganin[27] (used as a foundation for the superconducting leads). At 0.04°K the ratio of calorimeter heat capacity to Ho heat capacity was 1.7×10^{-2}. The uncertainity in this background heat capacity adds roughly $\pm 1\%$ to the total uncertainity of the Ho data at the extreme low-temperature end.

A minor problem was associated with the thermal switch coil which retained a remanent field from the adiabatic demagnetization cycle. Not only did this maintain the switch in the normal state, but the remanent field had a large gradient so that even a reverse bias current in the switch coil could produce only a small field-free, superconducting region in the tin. The solution was to initially center the large solenoid over the coil and magnetize, thus imposing a uniform remanent field which a bias current in the switch coil could readily cancel.[28] The samples were thus normally subjected to large fields before measuring C. The value of C, however, was never found to be a function of history, magnetic or otherwise, even though we were constantly on the alert for such behavior.

During a run the C were computed on a desk calcu-

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[24] A. G. Worthing and D. Halliday, *Heat* (John Wiley & Sons, Inc., New York, 1948), p. 111.

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

[26] N. G. Gliev and N. V. Volkenshtein, Fiz. Tverd. Tela **6**, 2560 (1965) [English transl.: Soviet Phys.—Solid State **7**, 2068 (1966)]; Zh. Eksperim. i Teor. Fiz. **49**, 24 (1965) [English transl.: Soviet Phys.—JETP **22**, 17 (1966)].

[27] J. C. Ho and N. E. Phillips, Rev. Sci. Instr. **36**, 1382 (1965).

[28] A. C. Anderson, W. R. Roach, and R. E. Sarwinski, Rev. Sci. Instr. **37**, 1024 (1966).

lator as the experiment progressed. Later the data were fed to a computer, at which time a correction for curvature was applied. This correction never amounted to more than 1%, and was normally ≈0.1%. In this paper a "run" refers to the period during which the cryostat was maintained below room temperature. During each run there were two or more adiabatic demagnetizations, and for each demagnetization two or more thermal cycles by means of the thermal switch and its control coil.

III. RESULTS

The polycrystalline Ho sample was of irregular shape except for two flat, parallel faces, and had a mass of 12.137 g (0.08358 mole). Our sample had been cut from a large piece which previously had been used in heat-capacity measurements above 0.4°K.[29] The vacuum-distilled material had been purchased from Research Chemicals, Inc. Spectrochemical analysis gave, by weight, 0.005% H, 0.07% C, 0.07% N, and 0.21% O; no other metals were detected. The only stable isotope of holmium is Ho^{165} with $I=\frac{7}{2}$. It crystalizes into a hcp structure, and is ferromagnetic below 20°K with a spiral structure of the electronic magnetic moments.[30]

The heat-capacity results are shown in Fig. 3. The data are listed in Table I. An earlier run produced data in good agreement with those of Table I, but they are not included because of a greater uncertainty in the thermometer calibration. Also included in Fig. 3 are data obtained by van Kempen *et al.*[5] and by Lounasmaa.[29] For the latter, only data above 0.6°K are shown because the data at the lowest temperatures are obviously in error. Measurements made by Gordon *et al.*[31] and by Dreyfus *et al.*[32] above 1°K are in good agreement with those of Lounasmaa. The data of van Kempen *et al.* appear to be systematically shifted to lower temperatures.

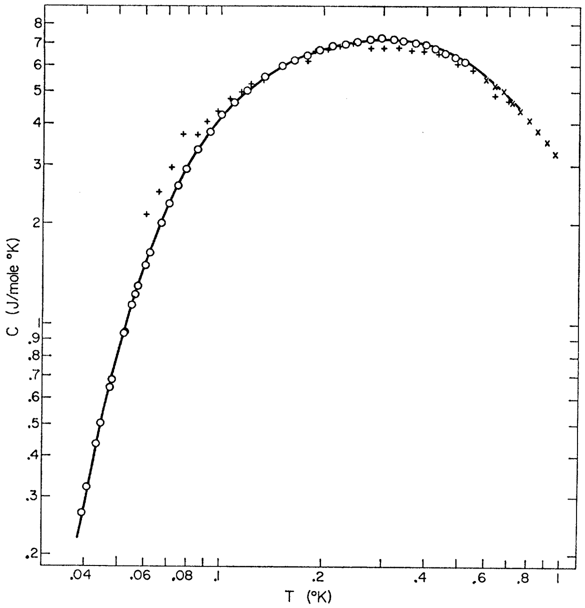

FIG. 3. Specific heat of Ho metal versus temperature. ○, present results; +, van Kempen *et al.* (Ref. 5); ×, Lounasmaa (Ref. 29). The "solid" line is our fit of a Schottky curve to the data.

The total heat capacity for the rare-earth metals may be written

$$C=C_L+C_E+C_M+C_N\,, \tag{3}$$

where the terms represent the lattice, electronic, magnetic, and nuclear contributions, respectively. For Ho, these become $C_E\approx 10^{-2}T$ and $C_L+C_M\approx 2.3\times 10^{-3}T^3$ J/mole °K as deduced by Lounasmaa from measurements made at higher temperatures.[29,33] Below 0.6°K, $C_N>0.99C$, so that within the accuracy of our data we measure only the nuclear contribution.

TABLE I. Measured specific heat of holmium metal in J/mole °K.

T(°K)	C	T(°K)	C
0.0409	0.321	0.1099	4.609
0.0449	0.503	0.1196	5.043
0.0482	0.681	0.1352	5.540
0.0523	0.938	0.1522	5.997
0.0565	1.233	0.1653	6.217
0.0603	1.496	0.1792	6.427
0.0395	0.268	0.1947	6.687
0.0435	0.436	0.2130	6.849
0.0477	0.646	0.2328	6.956
0.0525	0.947	0.2520	7.075
0.0553	1.135	0.2738	7.196
0.0575	1.295	0.2971	7.277
0.0622	1.640	0.3206	7.175
0.0673	2.009	0.3427	7.108
0.0710	2.296	0.3719	7.014
0.0751	2.596	0.4003	6.930
0.0797	2.929	0.4274	6.754
0.0859	3.335	0.4566	6.522
0.0935	3.779	0.4885	6.349
0.1011	4.251	0.5215	6.156

The polycrystalline Tb sample had a mass of 12.386 g (0.07793 mole) and also had been cut from a sample for which the heat capacity had been measured above 0.4°K.[34] The material had been purchased from Research Chemicals, Inc. Spectrochemical analysis gave, by weight, 0.02% H, 0.14% C, 0.01% N, and 0.12% O; no other metals were detected. The only stable isotope of terbium is Tb^{159} with $I=\frac{3}{2}$. It crystalizes into a hcp structure, and is ferromagnetic below 220°K with a spiral structure of the electronic magnetic moments.

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

[30] W. C. Koehler, J. Appl. Phys. **32**, 205 (1961).

[31] J. E. Gordon, C. W. Dempesy, and T. Soller, Phys. Rev. **124**, 724 (1961).

[32] B. Dreyfus, B. B. Goodman, A. Lacaze, and G. Trolliet, Compt. Rend. **253**, 1764 (1961); G. Trolliet, thesis, Grenoble (unpublished).

[33] J. A. Morrison and D. M. T. Newsham, in Proceedings of the Sixth Rare-Earth Conference, Gatlinburg, 1967 (unpublished), deduce somewhat different values for C_E and C_L+C_M from Lounasmaa's data. Their conclusions, however, are criticized by O. V. Lounasmaa and L. J. Sundström, Phys. Rev. **158**, 591 (1967).

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

The heat-capacity results obtained in three separate runs are shown in Fig. 4; the data are listed in Table II. Also shown on Fig. 4 are data from Lounasmaa *et al.*[34] and from van Kempen *et al.*[5] The agreement with the former is excellent. With the latter, the difference is probably within the combined errors of the two experiments,[35] although their data appear to be systematically shifted to higher temperatures. The results of Kurti and Safrata[36] agree above 0.5°K with the data of Fig. 4; the results of Heltemes and Swenson[37] above 0.25°K lie somewhat higher than the data of Fig. 4.

TABLE II. Measured specific heat of terbium metal in J/mole °K.

T(°K)	C	T(°K)	C	T(°K)	C
Run I				Run III	
0.0326	2.880	0.0709	5.387	0.0302	2.513
0.0361	3.280	0.0790	5.458	0.0322	2.844
0.0388	3.639	0.0872	5.449	0.0344	3.187
0.0419	4.035	0.0964	5.349	0.0368	3.490
0.0458	4.300	0.1044	5.304	0.0392	3.764
0.0502	4.642	0.1128	5.101	0.0419	4.023
0.0552	4.918	0.1193	5.039	0.0447	4.281
0.0604	5.103	0.1282	4.886	0.0476	4.520
0.0657	5.230	0.1379	4.618	0.0512	4.751
0.0760	5.426	0.1488	4.358	0.0557	4.959
0.0808	5.397	0.1544	4.123	0.0613	5.187
Run II		0.1612	4.041	0.0680	5.343
0.0278	2.104	0.1723	3.827	0.0750	5.422
0.0299	2.463	0.1836	3.575	0.0824	5.452
0.0301	2.485	0.1980	3.307	0.0908	5.442
0.0319	2.803	0.2105	3.043	0.1003	5.369
0.0332	2.987	0.2229	2.849	0.1107	5.193
0.0340	3.090	0.2285	2.728	0.1230	4.960
0.0361	3.397	0.2339	2.661	0.1378	4.590
0.0365	3.442	0.2419	2.590	0.1557	4.219
0.0388	3.731	0.2547	2.411	0.1760	3.729
0.0402	3.872	0.2633	2.285	0.1989	3.266
0.0419	4.065	0.2955	1.934	0.2065	3.170
0.0438	4.194	0.3179	1.698	0.2422	2.553
0.0453	4.377	0.3442	1.513	0.3015	1.871
0.0473	4.483	0.3708	1.327	0.3874	1.244
0.0488	4.613	0.4135	1.130	0.4687	0.897
0.0516	4.831	0.4510	0.958	0.1841	3.596
0.0524	4.841	0.4860	0.826	0.2115	3.057
0.0562	5.098	0.5413	0.696	0.2441	2.523
0.0574	5.046			0.2786	2.106
0.0634	5.245			0.3300	1.606
				0.4113	1.123
				0.3122	1.771
				0.3879	1.239

The various contributions to the heat capacity have been estimated[33,34] to be $C_L=0.58\times10^{-3}T^3$, $C_E=9.05\times10^{-3}T$, $C_M=0$, in units of J/mole°K, so that $C_N>0.99C$ below 0.6°K. Thus within the experimental accuracy we measure only C_N for Tb.

The measured entropy change provides a self-consistency check on the nuclear heat-capacity data. The spin entropy S associated with a Schottky curve for $2I+1$ nondegenerate levels is given by $S=R\ln(2I+1)$, where R is the gas constant. The measured increase in entropy for Ho from 0.0408 to 0.5206°K is 12.24 J/mole°K. Assuming a Schottky curve, then, would give 0.05 J/mole°K at $T\langle 0.0408$°K and 4.93 J/mole°K at $T\rangle$ 0.5206°K. The total entropy increase would then be 17.22 J/mole°K as compared to the theoretical value of $R\ln8=17.29$ J/mole°K, which is well within the ~1% uncertainty of the data. For Tb we measure an increase of 10.52 J/mole°K from 0.0278 to 0.5415°K. Assuming a Schottky curve fit at each end gives 0.61 J/mole°K at $T\langle 0.0278$°K and 0.37 J/mole°K at $T\rangle$ 0.541°K for a total of 11.50 J/mole°K. This is in excellent agreement with the theoretical value of $R\ln4=11.53$ J/mole°K.

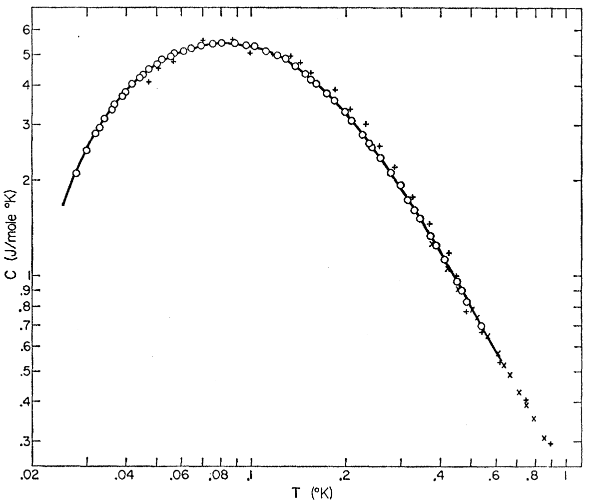

FIG. 4. Specific heat of Tb metal versus temperature. The data are from three different runs with separate thermometer calibrations. ○, present results; +, van Kempen *et al.* (Ref. 5); ×, Lounasmaa *et al.* (Ref. 34). The "solid" line represents both our fit of a Schottky curve to the data and the hyperfine parameters as determined from NMR measurements. For purposes of clarity, all points on this figure, as well as those of van Kempen and of Lounasmaa on Fig. 3, are the average of two experimental points.

The above calculations on entropy suggest that impurities (such as oxides) have little effect on our measurements of C_N. This argument is supported by the fact that, whereas specific-heat measurements on different samples are in rather good agreement below 1°K, obvious discrepancies associated with impurities are found to occur at higher temperature.[34,38]

There is little opportunity to compare our results with other techniques, since only neutron transmission has been done on Ho, and only NMR on Tb. The NMR in Tb did produce well-resolved lines which were consistent with $a'=0.1495$°K and $P=0.0161$°K.[39] The authors later found evidence that the NMR was in the bulk of the metal, not at domain walls as is usually assumed.[40] When the above values of a' and P are sub-

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stituted into Eq. (2) and C_N is computed the curve of Fig. 4 is produced. It may be seen that the present data are in excellent agreement with the NMR results. The neutron transmission data for Ho in the temperature range $0.05<T<4$°K gave $a'=0.305$°K and $P=0.002$°K.[40] When these values are substituted into Eq. (2) and C_N is computed, the results lie about 2% higher than the curve of Fig. 3 below 0.4°K, drop through the curve at 0.5°K, and lie about 7% below the data of Lounasmaa (and of Gordon *et al.*[31]) at 1°K. The disagreement between the calorimetric and neutron data appears to be outside the combined uncertainties even when considering the possibility pointed out by Brunkhart *et al.*[41] that the value of P obtained from neutron transmission may be too small because of a lack of thermal equilibrium.

If Schottky curves are fitted to our data, we obtain $a'=+(0.319\pm0.003)$°K, $P=+(0.004\pm0.001)$°K for Ho, and $a'=+(0.149\pm0.001)$°K, $P=+(0.0158\pm0.0005)$°K for Tb. In each case the sign of a' was determined from the electronic structure of the ion and the sign of the nuclear moment, whereas the sign of P was that required for the best fit to the data. These curves are plotted in Figs. 3 and 4, respectively. The fit for Ho is not as good as that for Tb, as indicated by the larger uncertainty limits. Nevertheless, it is obvious that the magnetic dipole and electric quadrupole interactions are sufficient to fit the data. A cooperative interaction which was suggested previously is not required to explain the data on Tb (see Sec. II).

It is possible to obtain theoretical values for the hyperfine interaction parameters a' and P, using as input data information from rare-earth ions in salts or from the free atoms. For Ho metal, Bleaney has calculated $a'=0.312$°K and $P=0.003$°K; and for Tb, $a'=0.152$°K and $P=0.029$°K,[4] with an estimated uncertainty of ±1%. Since direct measurements of some of the smaller contributions to the hyperfine fields have recently been made,[42] it may be possible to refine the theoretical estimates.

IV. CONCLUSION

Table III summarizes, in chronological order, the several determinations of the hyperfine parameters for Ho and Tb. There is quite good agreement between the various calorimeter measurements, even though one measurement for Ho only extended down to ~0.6°K. This reflects the fact that for these two metals the nuclear Schottky anomaly falls at rather high temperatures. Some confidence in the performance of the calorimeter[43] and in the accuracy of our data is provided by the good agreement between the measured and calculated entropies, and by the excellent agreement with the hyperfine parameters determined for Tb by means of NMR.

TABLE III. Summary of the hyperfine parameters for metallic Ho and Tb as found by various techniques.

Metal	Method	a'(°K)	P(°K)	Ref.
Ho	(theory)	0.312 ±0.003	0.003 ±0.0000	4
	calorimetric	0.320 ±0.010	0.007 ±0.0014	29
	calorimetric	0.320 ±0.005	0.008 ±0.0015	5
	neutron transmission	0.305 ±0.003	0.002 ±0.001	41
	calorimetric	+0.319 ±0.003	+0.004 ±0.001	present work
Tb	(theory)	0.152 ±0.0015	0.029 ±0.0003	4
	calorimetric	0.150	0.021	34
	calorimetric	0.152 ±0.002	0.013 ±0.004	5
	NMR	0.1495 ±0.00014	0.0161 ±0.0001	39
	calorimetric	+0.149 ±0.001	+0.0158 ±0.0005	present work

It has been noted that the nuclear hyperfine level structure for either Ho or Tb is well represented by the two parameters a' and P. The origin of the level splittings is not, however, completely understood, since there appears to be a real discrepancy between the theoretical and empirical values of the interaction parameters (Table III). The difference in a', for example, could be due to the polarization of core and conduction electrons by the 4f electrons. Although these contributions may tend to cancel each other, the effects are still sufficiently large to account for the apparent discrepancy.[4,42]

The parameters obtained for Ho^{165} in the present work correspond to the NMR frequencies 7.15, 6.98, 6.81, 6.65, 6.48, 6.31, and 6.15, in units of 10^9 Hz, which may be useful to those attempting to detect NMR in metallic Ho.

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