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THE SPECIFIC HEAT OF DYSPROSIUM METAL BETWEEN
0.4° AND 4°K

by

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TABLE OF CONTENTS

	<u>Page</u>
PREFACE.	5
I. INTRODUCTION.	7
II. PERTINENT THEORIES ABOUT SPECIFIC HEATS	8
Lattice and Electron Specific Heats	8
The Magnetic Specific Heat	8
The Contribution of Nuclear Spin Orientation to the Specific Heat.	9
The Total Specific Heat.	12
III. APPARATUS.	12
The Cryostat.	13
The Vacuum and He ³ Systems	14
The Calorimeter	15
The Carbon Thermometer	15
The Heater	16
The Magnetic Thermometer	16
IV. EXPERIMENTAL PROCEDURE	19
Measuring the Specific Heat.	19
Calibration of the Thermometers	20
Calculation of the Specific Heats.	21
V. RESULTS	22
VI. DISCUSSION	27
BIBLIOGRAPHY.	29

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Interior of Cryostat	13
2.	Cryostat and Vacuum System	14
3.	Mutual Inductance Bridge.	18
4.	Deviations of the Experimental Temperatures from the Mathematical Formula	21
5.	The Available Results on Dysprosium	25
6.	Empty Calorimeter.	25

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Experimental Results	23 & 24
2.	Constants in the Equation $C_p = At^3 + BT + CT^{3/2} + DT^{-2} + ET^{-3}$	28

PREFACE

This research was conducted in the Solid State Science Division of the Argonne National Laboratory while the author was a Resident Student Associate. He would like to express his great appreciation to his thesis advisors, Professor Paul L. Copeland of Illinois Institute of Technology, and Dr. Olli V. Lounasmaa of Argonne, for their guidance and encouragement. He also wishes to thank Dr. O. C. Simpson for the hospitality of the Solid State Science Division.

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I. INTRODUCTION

The low-temperature specific heats of most rare earth metals have, in addition to the usual lattice and electronic contributions, a component attributable to the electrons in the incomplete 4f shell. The effect of these electrons is twofold. There is the magnetic specific heat due to the interactions of unpaired electrons of different atoms and also the nuclear specific heat due to the interaction of the nuclear magnetic dipole and the electric quadrupole moments with the electrons of the atom.

A He^3 cryostat, which will be described here, was built at the Argonne National Laboratory to measure the specific heat of these metals. The first results, the specific heat of dysprosium from 0.4 to 4.2°K, will be discussed in Chapters V and VI.

Techniques for separation and purification of the rare earths have been the limiting factors in the exploration of their properties. These methods have now improved to the point where many of these materials are available commercially and in a state of quite high purity.

The study of the rare earths as a group is particularly interesting because they are similar in many ways. Almost all have the same crystal structure (hexagonal close packed) at low temperatures. The differences lie mainly in the size and electronic structure of the atoms, and in the number of 4f electrons. The electronic structures can be represented by a xenon core plus $(4f^n, 5s^2, 5p^6, 6s^2, 5d^1)$, where n goes from zero for lanthanum to 14 for lutetium. The outer electron configuration is thus the same, with the 6s and 5d electrons occupying the conduction band.

Temperatures of 1°K are easily reached by pumping on liquid He^4 . There are two ways to reach lower temperatures. One is the method of adiabatic demagnetization of a paramagnetic salt; the other is the use of a He^3 cryostat. Though magnetic cooling allows one to reach much lower temperatures than the 0.35°K reached with the use of He^3 , the He^3 cryostat has important advantages. One can cool larger samples, which helps in making accurate measurements, but mainly the He^3 cryostat is simpler and considerably more economical.

II. PERTINENT THEORIES ABOUT SPECIFIC HEATS

Lattice and Electron Specific Heats^{(1)*}

The low-temperature approximation of the Debye theory predicts that the specific heat due to the lattice, C_L , should be

$$C_L = (12\pi^4 R/5)(T/\theta)^3 \quad ; \quad (1)$$

here R is the ideal gas constant and θ is defined by

$$h\nu_m = k\theta \quad , \quad (2)$$

where ν_m is the maximum frequency of allowable elastic waves, h is Planck's constant, and k the Boltzmann constant.

In specific heat work the parameter θ , called the Debye temperature, is often used in representations of the data.

Aside from the term depending on T^3 , one encounters a linear dependence on T in the low-temperature specific heats of metals. This term is taken to represent the heat capacity of conduction electrons and is derived from Fermi-Dirac statistics. One will therefore refer to it as the electronic contribution, C_E , and it can be written as

$$C_E = BT \quad . \quad (3)$$

The Magnetic Specific Heat

In the analysis of more recent determinations of low-temperature heat capacities of ferromagnetic metals, a term proportional to the $\frac{3}{2}$ power of temperature is sometimes encountered. This term is usually referred to as the "spin wave term." The theory of spin waves is considered to be the most satisfactory way to deal with magnetism due to bound electrons at low temperatures.

In the case of ferromagnetic materials, the spins become polarized within a given domain and at low temperatures. If the temperatures are low enough, few spins face in a different direction. These spin deviations do not stay localized in the crystal but travel through the lattice as spin waves. If the number of deviations is small enough so that the interaction between the different spin waves can be neglected, then the magnetic specific heat can be calculated by the simple spin-wave theory.

* Reference to the bibliography will be made by means of superscripts in parenthesis.

This theory assumes that the magnetism is due only to electrons localized at stationary lattice points. The exchange energy is $-K \sum_{ij} \underline{S}_i \cdot \underline{S}_j$, where the $\underline{S}_i$ are the spin vectors and K is the exchange integral; the summation is extended over nearest neighbors only. When these effects are considered, the spin-wave theory yields the result

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

for the magnetic specific heat. Here c is a numerical factor which depends on the crystal structure.

Dysprosium is ferromagnetic below 85°K, so that one would expect the above to be applicable; one would expect the specific heat to contain a term of the form

$$C_M = C T^{3/2} \quad (5)$$

For details, see the review given by Kranendonk and Van Vleck.⁽²⁾

The Contribution of Nuclear Spin Orientation to the Specific Heat

At temperatures low enough that the electron spins are oriented, the nucleus is in a temperature-independent magnetic field H_{eff} .⁽³⁾ In this field a nucleus with angular momentum quantum number I will have $2I + 1$ spin orientations relative to the field. If the magnetic quantum number is m , then the energy is

$$E_m = -\mu H_{eff}(m/I) \quad (6)$$

where μ is the nuclear magnetic moment. From this, the partition function Z can be written as

$$Z = \sum_{m=-I}^{m=I} \exp(xm) \quad (7)$$

where

$$x = +\mu H_{eff}/kTI \quad .$$

From this, the specific heat can be calculated and is given by

$$C_N = -R x^2 \left[(2I+1)^2 \operatorname{csch}^2 \frac{(2I+1)x}{2} - \operatorname{csch}^2 x/2 \right] \quad (8)$$

For small x (temperatures not too low), one can use the expansion

$$C_N = R \frac{x^2}{3} \left[I(I+1) - x^2 \left\{ (2I+1)^4 - 1 \right\} / 80 \right] \quad (9)$$

Most results on low-temperature heat capacities showing a nuclear contribution have been analysed in terms of the last formula. Usually, only the first term has been used, since the temperatures have not been low enough for the next term to become large. An exception is provided by the specific heat of holmium, which was measured by Gordon, Dempsey, and Soller⁽⁴⁾ in the temperature range from 4 to 0.9°K. They used formula (9) because the nuclear magnetic moment of holmium is so large that the nuclear specific heat is sizeable at 4°K. Holmium, if measured at lower temperatures, should allow a severe check on the above formula and formulae of its kind.

Very convincing evidence that nuclei with magnetic moments do align themselves at low temperatures when in a magnetic field is the fact that radioactive atoms emit their radiation anisotropically when subject to these conditions.

Bleaney and Hill⁽⁵⁾ have predicted that the effects due to electronic quadrupole moment on the specific heat is not negligible when compared with the magnetic effects. The part of the Hamiltonian which depends on the orientation of the nucleus in the field of its electrons can be written as

$$H = VI_z + P [I_z^2 - (1/3) I(I+1)] \quad , \quad (10)$$

where V , which should vary as $\langle J_z - (1/3) J(J+1) \rangle$, is a measure of the magnetic interaction between the nucleus and the electrons, and P measures the quadrupole interaction. This Hamiltonian is valid if the gradient of the electric field is symmetric about the z axis.

Since the electrons are almost all polarized at low temperatures, one picks their direction of polarization as the z axis and one has $\langle J_z \rangle = J$ and $\langle J_z^2 \rangle = J^2$, so that V and P become constants which are effectively independent of the temperature in the region under study.

In a metal such as dysprosium, the axis of polarization is perpendicular to the crystal hexagonal axis. Since the gradient of the crystalline electric field is symmetric about this axis, another term is introduced into the Hamiltonian. In this case, the Hamiltonian is no longer diagonal in I_z . The contributions of these matrix elements are small and are neglected in the calculations.⁽⁶⁾

The part of the energy which depends explicitly on the magnetic quantum number can be written as

$$W_i = V(i-I) + P [(i-I)^2 - \frac{1}{3} I(I+1)] \quad , \quad (11)$$

where i takes on integral values from 0 to $2I$. The partition function is then

$$Z = \sum_{i=0}^{2I} \exp(-W_i/kT) \quad (12)$$

It can be expanded in powers of W_i/kT to yield

$$Z = \sum_{i=0}^{2I} \sum_{n=0}^{\infty} (-1)^n (W_i/kT)^n / n! \quad (13)$$

or

$$Z = \sum_{n=0}^{\infty} (-1)^n \overline{W^n} (2I+1) / n! (kT)^n \quad (14)$$

Here $\overline{W^n}$ is the average value of the n^{th} power of the energy levels. The first 3 terms of a power series for the specific heat then become

$$C_M/R = \overline{W^2}/(kT)^2 - \overline{W^3}/(kT)^3 - \left(\frac{3}{2} \overline{W^2}^2 - \frac{1}{2} \overline{W^4} \right) / (kT)^4 \quad (15)$$

The computation of the average values of the energy levels depends on the value of I . In dysprosium $I = 5/2$ and

$$\overline{W^1} = 0 \quad (16)$$

$$\overline{W^2} = (35/12)V^2 + (56/9)P^2 \quad (17)$$

$$\overline{W^3} = (56/3)V^2P + (160/27)P^3 \quad (18)$$

$$\overline{W^4} = (707/48)V^4 + (1300/9)V^2P^2 + (1568/27)P^4 \quad (19)$$

Of the five isotopes making up normal dysprosium, there are two, Dy^{161} and Dy^{163} , which have nuclear moments. Bleaney⁽⁶⁾ has given a list of the parameters for these isotopes. For Dy^{161} he gives $V = -820 \pm 20$ Mc/sec and $P = 150 \pm 30$ Mc/sec; for Dy^{163} he gives $V = 1140 \pm 20$ Mc/sec and $P = 180 \pm 30$ Mc/sec. Also, he gives the first term in

$$C_M = (26.6/T^2) - (1.32/T^3) - (0.12/T^4) \quad (20)$$

Here the relative concentrations (18.88 per cent for Dy^{161} ; 24.97 per cent for Dy^{163}) have been taken into consideration. The second and third terms were calculated with the help of equations (15) through (19). The values of V and P have been obtained from electron paramagnetic resonance experiments on dilute salts.

The nuclear contribution to the specific heat can also be calculated in closed form from the partition function as

$$C_N = \frac{R \sum_{i=0}^{2I} \sum_{j=0}^{2I} (W_i^2 - W_i W_j) \exp [-(W_i + W_j)/kT]}{(kT)^2 \sum_{j=0}^{2I} \sum_{i=0}^{2I} \exp [-(W_i + W_j)/kT]} \quad (21)$$

The Total Specific Heat

If one assumes that the previous discussion includes all the important ways in which the energy can distribute itself and that the different effects are independent, then one can write the total specific heat as a sum of the individual effects:

$$C_p = C_L + C_E + C_M + C_N + \delta \quad (22)$$

where δ is the work of deformation, which should be zero. In terms of temperature

$$C_p = AT^3 + BT + CT^{3/2} + DT^{-2} - ET^{-3} - FT^{-4} \quad (23)$$

III. APPARATUS

A He^3 cryostat used liquid nitrogen and liquid He^4 as the first cooling stages. By pumping on the He^4 , one reaches temperatures of about 1°K . At this temperature, the vapor pressure of He^4 tends to zero rather rapidly, so that further cooling by pumping is limited. On the other hand, the vapor pressure of He^3 is 8.6 mm Hg at 1°K , so that one can use He^3 as a coolant in the same way as He^4 and thus reach lower temperatures.

Once the sample is cooled to the lowest temperature, it is isolated by suspending it in vacuum with a silk thread. To determine the specific heat, a measured quantity of energy is added to the sample by passing a current through a resistance attached to the calorimeter.

A carbon thermometer was used to measure the temperature of the sample. In order to calibrate the carbon thermometer in the region in which the vapor pressure of He^3 becomes too small to be measured with a manometer (below 0.7°K), a magnetic thermometer was used.

The Cryostat

The cryostat was designed to have a minimum number of spaces in order to decrease the possibility of leaks. These spaces, shown in Fig. 1, are: the He^3 pot into which the He^3 is condensed where the magnetic thermometer is housed; the space below the He^3 pot, which contains the sample and is called the sample space; the space formed by the vacuum case surrounding these spaces, which is called the outer vacuum.

Fig. 1. Interior of Cryostat

of the bellows. The thread passes through a hole in the bottom of the He^3 pot, through the magnetic thermometer, and is attached to a steel wire. The wire goes through the thick pumping tube and is attached to the sample raising mechanism at the top of the cryostat. In this way the sample may be lifted without any He^3 escaping from the He^3 pot to the sample space.

The cryostat is inside a Dewar for liquid He^4 , and this Dewar is in turn surrounded by a liquid nitrogen bath (77°K).

At the top of the cryostat, the connections between the various tubes from the vacuum spaces and the lines coming from the pumps are made. The cryostat is fastened to an 8-ft aluminum tower so that the He^4 and nitrogen Dewars can be brought into position from the bottom.

Two pumping tubes, one of 0.5-in. and one of 0.1-in. diameter, terminate in the He^3 pot. Each of the other two spaces has a 0.1-in. pumping tube ending in it. These tubes are of thin-walled stainless steel which has a low heat conductivity.

Attached to the bottom of the He^3 pot are three copper rods which support the platform on which the sample rests during cooling. The platform is made of copper and is gold plated. To lift the sample, a silk thread is tied to the upper calorimeter cap and is attached to a bellows, which is closed at the lower end. The upper part of the bellows is soldered to the bottom of the He^3 pot, and another piece of thread is attached to the inside

The Vacuum and He³ Systems

From Fig. 2 it is evident how the vacuum system is connected. The tubing is copper, and the valves are of the bellows sealed type (Veeco).

The drawing is made so that the parts of the apparatus which have to do with pumping on spaces not containing He³ are at the right of the cryostat. A diffusion pump backed by a mechanical pump serves to evacuate all of the spaces which do not contain He³.

The Dewar which contains liquid He⁴ can be pumped on with a large mechanical pump capable of handling 120 cu ft of gas per minute. A 3-in. pumping line goes from the pump to the cryostat, but near the cryostat it narrows to 2½ in. The pumping is controlled by three parallel valves. The largest of these has a 3-in. diameter; the smallest is a needle valve.

The left part of the system depicted in Fig. 2 is for handling He³. The only interconnection between the left side and the vacuum system is via valve 15, which remains closed once He³ is in the system. The mechanical pump is specially constructed to be leak tight at the output side so that it is possible to recycle the He³ and to return it to the storage vessel.

Fig. 2. Cryostat and Vacuum System
vessel. The latter has a capacity of 6 liters.*

There are two pairs of manometers; one of each set is an oil manometer and one a mercury manometer. One set is used to measure the vapor pressure of He³ only; the other pair is used for He⁴. The manometers are read with a cathetometer.

*The rather large number of valves is necessary for making possible the various manipulations with He³. When the He³ has to be removed from the system, the Töpler pump is used to store all of the gas in the 6-liter container.

The fear that vibrations might spoil the experiments caused us to take a number of precautions. The cryostat and aluminum tower were isolated from the pumping lines by means of bellows or soft copper tubing which was bent in the shape of spirals. The mechanical pumps were isolated in a similar way. The mechanical vibrations due to the large pump were eliminated by bolting the large valve to a concrete pillar and having bellows of 2-ft length attached to both sides of this valve. The last 4 ft of the pumping line was a rubber hose.

The apparatus described here has many features in common with the He^3 cryostat of Seidel and Keesom.⁽⁷⁾

The Calorimeter

The calorimeter is made of copper and consists of two round caps which have threaded protrusions on the inside so that they can be screwed into the sample, which has threaded holes and is machined to fit the caps. The wall thickness of each cap is 0.015 in. so that their weight is quite small (8.9 gm).

The Carbon Thermometer

The carbon thermometer is made by first painting the side of the calorimeter bottom with General Electric resin (GE 7031) and baking it. Two, thin, insulated copper wires, 2 in. long, are run along the side of the calorimeter bottom and parallel to each other. These are fastened to the cap with resin, and the upper surfaces of the wires are filed to remove the insulation. Each wire is then covered with a narrow strip of silver paint (Du Pont No. 4817). After the paint is dry, an aqueous suspension of graphite (Acheson Colloids Co. Aquadag) is brushed onto the wires so as to form a conducting path, 2 cm wide, between the two strips of silver paint. When dry, the resistance between the wires should be about 100 ohms at room temperatures. This thermometer is very reliable; its response time is extremely short, and its resistance stays within convenient limits (140 ohms at 4°K, 820 ohms at 0.4°K).

Two leads are attached to the carbon thermometer. These wires pass out of the sample space through the He^3 pot and magnetic thermometer by a tube which terminates in a glass-to-metal seal containing 10 wires. The leads then go through the top of the outer vacuum via another glass-to-metal seal into the He^4 bath. At this point, each of them meets two wires which go to the potentiometer. One carries the current; the other is for measuring the potential. From the He^4 bath, they pass to the outside by an Amphenol adapter which is made leak tight with glyptol base paint. While inside the vacuum spaces the leads are made of tinned constantan in order to minimize thermal conductivity and eliminate Joule heat. The solder becomes superconducting below 4°K.

The current is supplied to the carbon thermometer by a 2-v battery and is limited to $2 \mu\text{a}$ by a series resistance of about 1,000,000 ohms. The current is determined by measuring, with a potentiometer, the voltage across a 1,000-ohm standard resistor.

The potentiometer is a six-dial, thermofree double potentiometer made by Minneapolis Honeywell (Rubicon Nr. 2773) and will subsequently be referred to as the large potentiometer. A photoelectric amplifier in conjunction with a galvanometer and a chart recorder serves as a null instrument. The six dials of the potentiometer make interpolation unnecessary. In the experimental setup, the lowest dial on the potentiometer corresponds to differences in potential of $0.01 \mu\text{v}$ and can easily be read. On the galvanometer the sensitivity is $30 \text{ mm}/\mu\text{v}$.

The Heater

The heater consists of about 2 ft of manganin wire which is wound noninductively around the top cap of the calorimeter and fastened to it by means of GE resin. The wires leading to it are similar to those of the carbon thermometer.

The heater current is supplied by a 2-v battery and is limited by a resistor which can be varied from 0 to 100,000 ohms in steps of one ohm. The magnitude of the current is determined by measuring the voltage across a 1,000-ohm standard resistor with another potentiometer (Rubicon Nr. 2781, later referred to as the small potentiometer).

The current through the heater is turned on manually and is turned off after a predetermined time by an electronic timer which uses the 60-cycle line frequency as the basic unit of time. A full-wave rectifier changes the alternating current to direct current with pulses every $1/120 \text{ sec}$. These pulses are formed into spikes and serve to operate the gate circuits of the timer. During the time in which the current does not pass through the heater, it is flowing through a variable resistor which is adjusted to have the same resistance as the carbon thermometer.

The Magnetic Thermometer

The fact that the susceptibility of paramagnetic salts is a function of temperature is the principle underlying the magnetic thermometer. The determination of this temperature dependence has been the subject of much theoretical work. Basic is the work of Van Vleck,⁽⁸⁾ who found the susceptibility of a spherical crystal to be of the form

$$x = \frac{C}{T + (\alpha/T) + \beta} \quad (24)$$

if the temperatures are not too low (a series expansion in powers of $1/T$ was involved). The calculation applies to a system in which the magnetic ions have cubic arrangement. Interactions between nearest neighbors and splittings of the energy levels due to the crystalline electric field were taken into account. The splitting can be determined from paramagnetic resonance experiments.

The salt used in the present thermometer is chromium methylamine alum in which there are 12 water molecules per molecule of alum. The constants α and β are given by Durieux⁽⁹⁾ as 0.00279 ($^{\circ}\text{K}$)² and 0.010°K , respectively.

A sphere is prepared by mixing the salt with GE resin and casting the mixture into a cylindrical shape. The cylinder is then scraped and filed until a sphere of 0.5-in. diameter is formed. A hole, one millimeter in diameter, is drilled through the salt pill to allow passage of the silk thread which lifts the sample.

The magnetic thermometer has a secondary and a primary coil. Two thousand turns of 0.005-in. niobium wire which is wound on a Lucite spool make up the primary. Because niobium becomes superconducting at low temperatures, no Joule heat will be developed. At room temperatures, the resistance of the primary is about 800 ohms; at low temperatures, the resistance is due to the leads only and is about 2 ohms. The secondary consists of copper wire (gauge 40) wound on a Lucite spool which fits inside the primary. There are two sections to the secondary. Each of them has about 2,000 turns. They are wound to oppose each other and are connected in series. When the secondary is inside the primary, the mutual inductance should be due to the magnetic material only, since the sphere is centered in the lower section of the secondary.

The salt pill is glued into the bottom of the magnetic thermometer.

The primary fits inside a Lucite cylinder which, in turn, fills up most of the He^3 pot. The leads going to the magnetic thermometer enter the large center tube at the top via a glass-to-metal seal. These leads are of copper down to about 8 in. from the He^3 pot, where they are attached to a radiation shield. From there on, the wires are of niobium so that the heat brought to the He^3 pot is minimized.

Connections between the copper and niobium wires were made by painting the cleaned ends with silver paint and sticking them into a short piece of thin copper tubing. The tube was then crimped to hold the wires in place.

The measuring circuit is in principle the Hartshorn bridge for impure inductances.⁽¹⁰⁾ A variation, shown in Fig. 3, in which a phase-

shift potentiometer is employed is used. In order to keep capacitive effects to a minimum, an oscillator of low frequency was selected; in order to filter out the 60-c/sec line frequencies effectively, it was operated at 13 c/sec. The output of the oscillator was kept at about 7.5 ma. The arrangement of the components can be seen from the drawing. The phase-shift potentiometer is the group of three resistors; R varies from 0.1 to 1,000 ohms, and r_s and r_p vary from 0.1 to 10 ohms.

The mutual-inductance box is a variable mutual inductance made according to the specifications and instructions given by Wolf.⁽¹¹⁾ It has five decades so that the mutual inductance can be read to five significant figures. The advantages of this piece of equipment are its insensitivity to the proximity of metals and electromagnetic fields, and its simple construction.

Fig. 3. Mutual-inductance Bridge

The switches s_1 , s_2 , and s_3 are reversing switches. In the experimental bridge, this switch is a six-pole, eleven-position, rotary switch. It is wired so that all possible combinations of polarity can be selected.

In order to balance the bridge, both the real and imaginary parts of the mutual inductance of the magnetic thermometer must be compensated. The real part is balanced with the mutual-inductance box; the imaginary part is balanced by adjusting the phase-shift potentiometer.

The amplifier, together with the oscilloscope, serves as the null instrument. A reference signal, taken directly from the oscillator, is placed on the horizontal plates; the output from the amplifier is placed across the vertical plates of the oscilloscope.

The phase of the signal which is fed into the primary circuit can be changed at the oscillator. The phase difference between reference and primary voltage is adjusted so that a variation of the mutual-inductance

box settings changes the amplitude of the elliptical scope trace; varying the resistor R rotates the trace (r_p is kept equal to r_s and they are seldom changed). When the ellipse degenerates into a horizontal line, the bridge is balanced. The null instrument can detect changes in potential of 10^{-8} v.

IV. EXPERIMENTAL PROCEDURE

Measuring the Specific Heat

After one has cooled the apparatus to liquid nitrogen temperatures, all exchange gas is removed from the sample and outer vacuum spaces by pumping for at least 12 hr until a leak detector shows a very small helium reading. One then pumps on the He^4 bath until a temperature of 1.15°K is reached and condenses the 5 liters of He^3 gas into the He^3 pot. When a temperature of 1.15°K is again reached, one commences to pump on the He^3 with the mechanical and diffusion pumps. After about 2 hr, the He^3 pot reaches a temperature of about 0.33°K , and this temperature can be maintained for about 48 hr without recondensing.

The cooling of the sample takes much longer; it took 17 hr to cool dysprosium from 1.1 to 0.4°K . The He^4 Dewar had to be refilled every 12 hr, but this did not significantly affect the temperatures of the He^3 pot.

When the lowest experimental temperature has been reached, the sample, which has been setting on the platform during cooling, is lifted and the drifts are observed by taking readings of the carbon thermometer and recording the time at which they are taken. Next, current I_H is passed through the heater by activating the timer and is measured with the small potentiometer. A heating period, t , lasts about 60 sec; the current varies from 0.3 to 1.5 ma and is chosen so as to space the specific heat points approximately 0.1°K apart. After about 10 sec, the sample comes to equilibrium and the after-drift serves as the fore-drift for the next specific heat point. For dysprosium, the drifts were $20 \mu^\circ\text{K}/\text{min}$ at 1°K and $200 \mu^\circ\text{K}/\text{min}$ at 4°K , and thus were hardly noticeable.

In order to calculate the heat input, one has to know the heater resistance R_H . It was measured with the large potentiometer at various temperatures between 0.4 and 4.2°K , and was found to be expressible as

$$R_H = (361.91 + 0.03 T) \text{ ohms} \quad . \quad (25)$$

Thus the heat input ΔQ can be computed from the relation

$$\Delta Q = I_H^2 R_H t \quad . \quad (26)$$

Calibration of the Thermometers

The most time-consuming part of the experiment is the calibration of the thermometers. This must be done after the specific heat measurements without allowing the carbon thermometer to warm above 4.2°K, since it then would change its thermometric properties. The thermometer was calibrated after every group of experiments by means of the following sequence:

1. Between 2.2 and 0.75°K the vapor pressure of He³, measured through the large tube from the pot, was employed as the primary thermometer. The smaller tube was used for pumping in order to keep the temperature constant; to make sure that the He³ pot and sample were in thermal equilibrium, He³ exchange gas was used in the sample space. When the readings of the thermometers were very steady, the vapor pressure of the He³ was taken and recorded, together with the corresponding values of the carbon and magnetic thermometers. The tables of Sydoriak and Roberts⁽¹²⁾ [recalculated to the T₅₈ scale⁽¹³⁾] were used to evaluate the temperatures. A correction for the 0.6% of He⁴ in the He³ gas was applied.

2. Between 0.75 and 0.4°K, the magnetic thermometer was used as a primary thermometer. Since the susceptibility is given by equation (24), one expects the mutual inductance X to be of the form

$$X = A + \frac{B}{T + (0.0028/T) + 0.01} \quad , \quad (27)$$

where the constants A and B can be determined by least-squares analysis based on values of T and X above 0.75°K. The sensitivity of the measuring system was 0.1 millidegree at 1°K. The use of a magnetic thermometer makes vapor pressure measurements below 0.75°K unnecessary, and corrections due to the thermomolecular pressure difference are avoided.

3. From 4.2 to 2.2°K, the carbon thermometer is calibrated against the vapor pressure of He⁴. For this purpose, a quantity of about 40 cc of He⁴ were condensed into the sample space. By pumping on the He⁴ through the tube leading to the sample space to establish equilibrium and measuring the vapor pressure through the same tube, one can calibrate in this region. One cannot use this method to go below 2.2°K, because the evaporation of He⁴ increases markedly at the lambda point and large pressure gradients develop in the pumping line. The apparatus was built so that one can also measure the vapor pressure of the He⁴ bath. This allowed one to see if the He³ and He⁴ scales gave the same result. The vapor pressure as determined from the Dewar is useful only below the lambda point since, because of the large heat conductivity of the superfluid the He⁴ in the Dewar can come to equilibrium. Temperatures were determined according to the T₅₈ scale.⁽¹³⁾

The carbon thermometer was calibrated at 30 points over the whole temperature range. The results were fitted to an equation of the type

$$1/T = aR^{-2} + bR^{-1} + cR^{-1/2} + d + eR^{1/2} + fR \quad , \quad (28)$$

where R is the thermometer resistance and $a, \dots, f$ are constants. This equation was used to calculate temperatures.

Fig. 4. Deviations of the Experimental Temperature from the Mathematical Formula

Figure 4 shows a typical deviation plot from the mathematical curve. The scatter is generally less than 2 millidegrees, and the He^3 and He^4 points join smoothly. The calculated temperature is thus probably within one millidegree of the temperature defined by the He^3 and He^4 scales. Uncertainties of about 2 millidegrees can arise from the extrapolation of the magnetic thermometer to temperatures below 0.75°K .

Depending on their magnitude, the vapor pressures were measured with either oil (di-n-butyl phthalate) or mercury manometers. Corrections due to location of the laboratory (gravitational attraction), and changes in the density of the manometer liquids with temperature were made. Also, the temperature dependence of the glass scale of the cathetometer was taken into account. Since the tubes of the manometers were not of exactly equal diameters, a small correction due to capillary action was applied to the data read from the mercury manometers: -0.05 mm for the He^4 and -0.04 mm for the He^3 manometer.

Calculation of the Specific Heats

In order to compute the mean specific heat $\bar{C}_p$ one must know the temperature difference caused by the heating. When the temperature is plotted as a function of time, the drift points are expected to lie on a straight line; these lines are extrapolated to the center of the heating period and the difference in temperature between the fore- and after-drifts, ΔT , is evaluated at that point. The mean specific heat is then

$$\bar{C}_p = \frac{\Delta Q}{\Delta T} \quad , \quad (29)$$

and the temperature at which this point is located will be taken as the temperature $\bar{T}$ half-way between the fore- and after-drifts when evaluated at the middle of the heating period.

The specific heat is, of course, a point function defined as

$$C_p = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} = \frac{dQ}{dT} \quad (30)$$

To find the coefficients in formula (23), which is an equation for C_p as a function of T , one must transform this equation into a function of $\bar{C}_p$, $\bar{T}$, and ΔT , the known parameters.

In general, if the specific heat is known to be expressible as

$$C_p = \sum_i U_i T^{n_i} \quad (31)$$

where $n_i \neq -1$, then

$$\bar{C}_p = \frac{\int_{\bar{T} - \frac{\Delta T}{2}}^{\bar{T} + \frac{\Delta T}{2}} C_p dT}{\Delta T} = \frac{1}{\Delta T} \sum_i \frac{U_i [(\bar{T} + \Delta T/2)^{n_i+1} - (\bar{T} - \Delta T/2)^{n_i+1}]}{n_i + 1} \quad (32)$$

Using the data, one can find the coefficients U_i by least-squares analysis. For more details of the calculations, which were done on an IBM 704 digital computer, see the description of the program by Roach.⁽¹⁴⁾

V. RESULTS

The dysprosium sample was prepared by Research Chemicals (Division of Nuclear Corporation of America). It was vacuum distilled, remelted in vacuum, and cast into a tantalum crucible. The tantalum was then machined off and the sample was formed into a cylinder, 5.0 cm long and 3.2 cm in diameter. After the threaded holes had been made at both ends, the sample weighed 256.66 gm (1.5794 moles). The following impurities were detected: tantalum, 0.03%; oxygen, 0.08%; and hydrogen, 0.03%. No other metals were detected by spectrochemical analysis.

A tabulation of the experimental results is given in Table 1, and most of the points are plotted in Fig. 5. From the graph one sees that the specific heat rises sharply below 1°K - one finds the expected nuclear specific heat. One sees an anomalous hump centered about 2.35°K.

Table 1

EXPERIMENTAL RESULTS

T(°K)	C _p (mJ/mole-°K)	T(°K)	C _p (mJ/mole-°K)
<u>Run IA</u>		<u>Run IB</u>	
0.5822	81.89	0.4241	128.09
0.5942	79.52	0.4559	116.24
0.6107	76.38	0.4949	103.80
0.6279	73.47	0.5429	90.77
0.6459	69.92	0.5928	79.83
0.7104	61.74	0.6504	69.68
0.7317	59.19	0.7220	60.27
0.7538	57.02	0.7967	53.25
0.7885	53.10	0.8729	48.18
0.8371	50.38	0.9562	44.59
0.8888	47.44	1.0451	42.21
0.9435	45.09	1.1375	41.09
1.008	43.20	1.2310	41.16
1.0600	41.93	1.3325	42.16
1.1205	41.26	1.4395	44.12
1.1927	41.01	1.5492	46.95
1.2754	41.60	1.2893	41.69
1.3568	42.57	1.3982	43.28
1.4491	44.26	1.5101	46.01
1.5505	46.87	1.6395	50.06
1.6574	50.46	1.7941	56.16
1.7832	55.38	1.9513	63.98
1.9465	63.46	2.1149	73.33
2.1882	75.52	2.3164	79.77
2.4924	79.02	2.5669	79.75
		2.8429	85.75
<u>Run IC</u>		<u>Run IIA</u>	
0.7075	62.12		
0.7738	55.28	1.3656	42.75
0.8476	49.73	1.4217	43.89
0.9287	45.59	1.4856	45.16
1.0159	42.88	1.5555	47.18
1.1075	41.44	1.6292	49.47
1.2009	41.06	1.7055	52.33
1.2941	41.61	1.7846	55.80
1.3852	42.94	1.8663	59.35
1.4810	45.08	1.9518	63.54
		2.0416	68.76

Table 1 (Cont'd.)

T(°K)	C _p (mJ/mole-°K)	T(°K)	C _p (mJ/mole-°K)
<u>Run IC (Cont'd.)</u>		<u>Run IIA (Cont'd.)</u>	
1.5858	48.14	2.1353	74.12
1.6954	52.02	2.2322	78.28
1.8174	57.16	2.3331	80.38
1.9624	64.49	2.4404	79.87
2.1308	74.14	2.5533	80.30
2.3317	79.23	2.6701	82.17
2.5670	79.46	2.7876	84.98
2.8206	85.11	2.9065	88.55
0.4266	127.12	3.0242	93.26
0.4582	115.49	3.2673	102.12
0.4931	104.25	3.3897	106.47
0.5320	93.41	3.5123	110.53
0.5754	83.33	3.6410	115.49
0.6242	73.91		
0.6792	65.54		
<u>Run IIB</u>		<u>Run III</u>	
3.0658	94.62	2.2947	78.49
3.1885	99.07	2.4207	78.74
3.3131	103.43	2.5522	78.80
3.4417	108.05	2.6872	81.83
3.5750	112.54	2.8227	85.68
		2.9577	89.74
		3.0945	94.54
		3.2352	99.61
		3.3801	104.78
		3.5308	110.73
		3.6899	117.09
		3.8566	123.78
		4.0341	130.33

The heat capacity of the empty calorimeter was measured between 1.4 and 4°K in a separate experiment. Rayne⁽¹⁵⁾ has measured the specific heat of copper between 0.2 and 1°K, and found that it consists of a lattice and an electronic contribution only. Since the bulk of the calorimeter is copper, one expects to be able to represent its heat capacity, C_{cal} , as

$$C_{cal} = A_{cal} T^3 + B_{cal} T \quad . \quad (33)$$

Analysis of the data gave $A_{cal} = 0.0081 \text{ mJ/}^\circ\text{K}^4$ and $B_{cal} = 0.116 \text{ mJ/}^\circ\text{K}^2$. Since C_{cal} is always less than one per cent of the total heat capacity of dysprosium, the uncertainty in this quantity is of no consequence. If one plots C_{cal}/T against T^2 , formula (33) represents a straight line. Figure 6 shows a plot of the data on such a graph.

Fig. 5
The Available Results for
Dysprosium

Fig. 6
Empty Calorimeter

Two separate experiments were done with dysprosium. The data marked Run IA, IB and IC in Table 1 were from the first experiment. The whole temperature range was traversed three times. The data marked

Run II and Run III were the results from the second experiment and cover only the upper part of the temperature range under consideration. Within each run, the random scatter of the experimental points was only 0.1 per cent. This is partly due to the good thermal isolation of the sample and to the fact that after each heating period equilibrium is reached in a very short time. Systematic errors in timing, heating current, and heater resistance amount to no more than 0.2 per cent in the final results.

The experimental accuracy was limited mainly by the thermometer calibrations. Aside from possible errors in the temperature scale, the accuracy of the present results is estimated as 1% between 0.8 and 4°K, and somewhat better than 2% at 0.4°K. The larger error at the lowest temperatures is due to the rapid variation of the specific heat as a function of temperature and to the extrapolation of the temperature scale with the magnetic thermometer.

Separation of the measured specific heat into contributions according to (23) is difficult because of the anomaly, and so it was decided to omit the points between 1.2 and 3.5°K from the analysis. Also, since the data by Dreyfus, Goodman, Trolliet, and Weil⁽¹⁶⁾ show neither magnetic specific heat nor anomaly for one of their samples (sample A, see Fig. 5), their value for A, 0.22 mJ/mole-°K⁴, was adopted. The constants $E = 1.32 \text{ mJ-°K}^2/\text{mole}$ and $F = 0.12 \text{ mJ-°K}^3/\text{mole}$ were calculated from formulas (15) through (19) with the use of data given by Bleaney.⁽⁶⁾ The constants A, E, and F were then treated as predetermined constants in the least-squares analysis. The results, with the specific heat in mJ/mole, are: $B = 9.5 \pm 0.9$, $C = 9.7 \pm 0.5$, and $D = 26.4 \pm 0.1$. The limits of error are statistical only.

The calculated specific heat is shown in Fig. 5. Below 1.2°K, the experimental points fit this curve to within one or two per cent. The temperature dependences of C_E and C_M are so similar that the two contributions cannot be separated very accurately; the nuclear specific heat, on the other hand, is so predominant below 1°K that it can be determined with higher precision. The values of B and C are estimated to be correct within 10% and the value of D within 2%.

The absence of a magnetic specific heat in the data of Dreyfus, Goodman, Trolliet, and Weil⁽¹⁶⁾ made one suspect that the specific heat depends on the rate at which the sample is cooled from room temperature, especially since experiments with other rare earths have shown that the specific heat depends on the time the sample spends in the region near the Curie point.^(17,18) To test this, Runs II and III were undertaken. In Run II the sample was cooled from room temperature to 4.2°K in 30 hr with the heat switch (conduction) only; in Run III, the same temperature interval was covered in $1\frac{1}{2}$ hr by the use of exchange gas. No differences were observed in the specific heat.

VI. DISCUSSION

All the available specific heat data for dysprosium in the temperature range from 0.4 to 4°K have been plotted in Fig. 5. The first measurements of the specific heat of dysprosium were made by Dash, Taylor, and Craig.⁽¹⁹⁾ They covered the temperature interval from 0.25°K to 2°K, but their data showed a very large hump above 0.5°K. At the recent Rare Earth Conference (Glenwood Springs, Colorado, September, 1961) measurements by Parks⁽²⁰⁾ as well as the present results were presented. At about the same time, in France, data by Dreyfus, Goodman, Trolliet, and Weil⁽¹⁶⁾ were published.

At the lower temperatures the agreement between the various results is fairly good, possibly within the experimental errors. The results of Parks agree best with the present work at temperatures below 1°K. In this region, Dreyfus, Goodman, Trolliet, and Weil⁽¹⁶⁾ give only six points, which somewhat limits the accuracy of their evaluation of the nuclear term.

At higher temperatures, the agreement between different measurements is very poor; Fig. 5 speaks for itself. All the data, except sample A by Dreyfus, Goodman, Trolliet, and Weil,⁽¹⁶⁾ show humps. The most convincing explanation for these is that they are due to oxygen impurities. This is supported by the work of Crane,⁽²²⁾ who showed that when the oxide impurity in gadolinium is increased from 0.11% to 0.22% the specific heat at 2°K becomes greater by 70%. The sample of Parks⁽²⁰⁾ had an oxygen content of 0.13%, as compared with 0.08% in the present sample. The other workers did not give the oxygen contents of their specimens.

It was suggested by Dreyfus, Goodman, Trolliet, and Weil⁽¹⁶⁾ that the anomalies may be due to tantalum impurities. This explanation may not be correct since their sample A, which exhibited no anomaly, had a tantalum concentration of 0.05%, which may be compared with the tantalum content (0.03%) of the present sample. It may be that the anomaly is not of the Schottky type, since it decays quite rapidly at the higher temperatures; it is probably cooperative in nature.

Different oxide impurities are apparently not the whole explanation for the divergent results. It is possible to represent the present results and the work of Parks⁽²⁰⁾ by equation (23), where (C_p in mJ/mole) $A = 0.22$, $B = 9.5$, $D = 26$, and $C = 9.7$ and 27 , respectively. This leads one to suspect that the discrepancies at the higher temperatures are partly due to a magnetic specific heat. The reason for the difference is not known.

By putting $K = 1.91$,⁽²¹⁾ $c = 0.028$ (h.c.p. lattice), and $S = 5/2$ in (6), the spin wave theory gives $C = 7.9$ mJ/mole-°K^{5/2}. Measurements by Skochdopole, Griffel and Spedding⁽²³⁾ between 15 and 300°K indicate that

the magnetic entropy at 20°K is 550 mJ/mole-°K, which, if a $T^{3/2}$ -dependence for C_M assumed below 20°K, would give $C = 9.2$ mJ/mole-°K $^{5/2}$, a value agreeing well with the present results.

Values of the constants in equation (23) determined by different investigators are given in Table 2. The lattice specific heat as given in the French paper⁽¹⁶⁾ corresponds to a Debye temperature $\theta = 207^\circ\text{K}$. This is considerably larger than $\theta = 158^\circ\text{K}$ as deduced from high-temperature measurements⁽²⁴⁾ which correspond to $A = 0.49$ mJ/mole-°K. This was the value of A adopted by Parks in the analysis of his data. There is good agreement on the value of B , as can be seen from Table 2. When calculating D , the other experimenters did not take into account terms of higher order, so that their values of D would increase by 14%. If this is taken into consideration, the results of Parks agree rather well with the present work.

Table 2
CONSTANTS IN THE EQUATION

$$C_p(\text{mJ/mole-}^\circ\text{K}) = AT^3 + BT + CT^{3/2} + DT^{-2} - ET^{-3} - FT^{-4}$$

Author	A	B	C	D	E	F
Present work	0.22	9.5	9.7	26.4	1.32	0.12
Dash <i>et al.</i> ⁽¹⁹⁾	0.75	10	0	20	0	0
Parks ⁽²⁰⁾	0.49	9.2	22	22	0	0
Dreyfus <i>et al.</i> ⁽¹⁶⁾	0.22	9.0	0	30	0	0
Bleaney ⁽⁶⁾	-	-	-	26.6	1.32	0.12

At the lowest experimental temperature, 0.4°K, the terms ET^{-3} and FT^{-4} contribute 12% and 3%, respectively, to the nuclear specific heat. If these terms are ignored in the analysis, the fit becomes poorer. This indicates that the quadrupole contribution to the specific heat is important.

The value of 9.5 mJ/mole-°K 2 for the coefficient in the electronic specific heat of dysprosium can be compared with the experimental results $B = 10.1$ for lanthanum,⁽²⁵⁾ 12.1 for samarium,⁽¹⁷⁾ and 9.5 for lutetium.⁽²⁶⁾ It seems, therefore, that C_E is similar for all these rare earths. However, recent measurements by Dreyfus, Goodman, Lacaze, and Trolliet⁽²⁷⁾ give the coefficient B for Pr as 19.0, for Ho as 26, for Er as 13, and for Tm as 21.5, where the specific heat has the units of mJ/mole-°K. The measurements have been reported very briefly, but, since the magnetic specific heat was ignored, it may be that these values are too high. These authors had thus assumed that the electronic spins are completely oriented at these low temperatures.

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