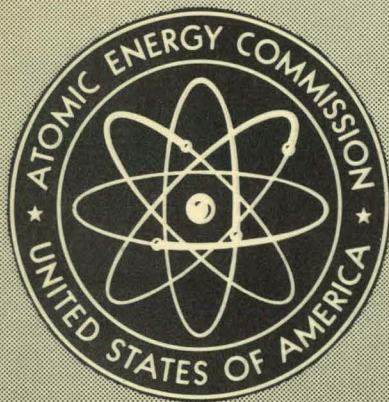


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ZERO FIELD MAGNETIC PROPERTIES OF
GADOLINIUM, TERBIUM AND SAMARIUM

By
Emma Daniels Hill
F. H. Spedding

November 1960

Ames Laboratory
Iowa State University
Ames, Iowa

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ZERO FIELD MAGNETIC PROPERTIES OF GADOLINIUM, TERBIUM AND SAMARIUM*

By

Emma Daniels Hill and F. H. Spedding

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ABSTRACT

The mutual inductance due to the presence of the sample in a coaxial, cylindrically wound inductance coil, has been observed for gadolinium, terbium and samarium in fields of a few oersteds over the temperature ranges 78 - 310°K, 78 - 235°K and 4.2 - 150°K. This mutual inductance might be referred to as an apparent susceptibility although a direct relationship between this apparent susceptibility and a static susceptibility is neither obvious nor presently calculable.

The dynamic mutual inductance method was used and the results have been compared with other work reported in the same temperature ranges. The rise in the mutual inductance curve for gadolinium occurred in the temperature region 270 - 295°K. An extrapolation of data in the high temperature region yielded a paramagnetic Curie point of 284.2°K which is 5° lower than the reported value. The transition in terbium occurred to within a degree of the predicted temperature of 220°K and a second peak occurred at 229.4°K which is within 2° of the heat capacity peak. The peak at 220°K was found to exhibit hysteresis and time-dependence. No hysteresis was observed in the peak of the ΔM versus T curve for samarium at 14.8°K; but the low temperature peak occurred at a temperature which differed by only 0.1° from that reported in other magnetic work, while by the same method no anomaly of appre-

*This report is based on an M.S. thesis by Emma Daniels Hill submitted November, 1960, to Iowa State University, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

ciable size was detected at higher temperatures to compare with that of heat capacity data. An extrapolation of ΔM versus T to $\Delta M = 0$ in the region $230 - 235^{\circ}\text{K}$ yielded a Curie point of 235.6°K .

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Improvements in this work might be made in several ways. One would be to extend measurements to higher temperatures to see if a plot of $1/\Delta M$ versus T would yield a straight line and how well the value of Θ obtained from such a plot compared with reported values. Another would be to use a sample of known χ to calibrate the apparatus so that absolute values of χ for an unknown could be calculated above the Curie point. A thorough examination of the resistive component obtained by this method would be beneficial especially if it could be quantitatively related to irreversible magnetization effects in the region of a transition. A measurement of the change in inductive and resistive components as a function of frequency should also be helpful in explaining these irreversible effects.

INTRODUCTION

The rare earths have for many years been of particular interest because the presence of the partially-filled 4f shells in these elements provides an excellent opportunity for studying these shells in the solid state under conditions similar to those prevailing in the free atom. It was only in the past few years that an effective method of separation based on the ion-exchange process was developed (16) and only during this time have rare earths of high purity been generally available for study. Although a considerable amount of work, including measurements of specific heat, magnetic susceptibility, resistivity, thermoelectric power and other properties, has been done on the rare earths, there is still much to be done in explaining the physical properties of these elements.

Some of the rare earths have been found to be ferromagnetic and/or antiferromagnetic below room temperature. Studies of their specific heats, resistivities and magnetic susceptibilities have shown that the rare earths exhibit anomalous behaviors in the region of and below their Curie or Neel temperatures. In the case of ferromagnets, it has been shown that below the Curie temperature, a large magnetic saturation can exist even in nearly zero applied fields. According to domain theory (10) any microscopic region of such a material is saturated in zero field, where the spins

tend to align parallel, but the overall magnetization is much lower than this in general because of the existence of domains. Since all magnetic measurements which have been made so far have been in relatively large applied fields, it was deemed advisable to carry out some magnetic measurements in very small fields.

In the work which will be presented here, the dynamic mutual inductance method has been used to make magnetic measurements in fields of only a few oersteds. Essentially, the method involves placing a sample in a cylindrical coaxially wound mutual inductance coil, and measuring the change in mutual inductance between the primary and secondary due to the presence of the sample. These measurements are carried out as a function of sample temperature. Although the results of mutual inductance measurements cannot be directly related to the magnetic moment below the Curie point because of the movement of domain walls, the mutual inductance method is valuable in that it provides easy access to the study of magnetic transitions in very small applied fields over the temperature range 1.3-300°K. These data are in some ways more sensitive to zero field temperature and time hysteresis effects than are heat capacity and resistivity data. They may be correlated with magnetic and thermal data to confirm the existence of magnetic transitions in metals and give detailed, though as yet noninterpretable, descriptions of

their temperature-time behavior. Thus, the data may prove to be valuable in the event a quantitative description of domain wall movement, as a function of varying field and temperature, is developed.

Trombe first reported the ferromagnetic properties of gadolinium in 1935. This metal was found to become ferromagnetic below 289°K (13). Specific heat measurements (6), resistivities (3), magnetic studies using large applied fields (4) and measurements of the thermoelectric power (2) as a function of temperature, have been made on this metal and substantiate the fact that gadolinium does indeed become ferromagnetic in the temperature region of 289°K .

Terbium, like gadolinium, also is known to become ferromagnetic (17). Specific heat measurements (9) indicated a ferromagnetic transition around 220°K . The magnetic properties in large applied fields (17) as well as the resistivity (3) and thermoelectric power (2) of terbium have also been studied.

Samarium is curious in its behavior because of its unique crystal structure and its tendency to exhibit divalent as well as trivalent behavior. Lack of agreement in specific heat measurements (8, 15) prompted the thought that this metal might also become ferromagnetic in the region of the low temperature specific heat anomaly. Magnetic properties of samarium have been studied (14) but only in large applied

fields. The resistivity (3) and thermoelectric power (2) as a function of temperature have also been studied.

MATERIALS AND APPARATUS

Materials

The methods of preparation of gadolinium (6), terbium (9) and samarium (8) were the same as described previously. Reports of spectrographic analysis for each metal were as follows:

Gadolinium	.02% Fe; .1% Ta; .02% Mg; .05% Dy; .01% Y; <.01% Eu; <.01% Tb; <.03% Nd; <.05% Ho; <.02% Sm; Ca, not detected
Terbium	.05% Sm; .02% Y; .01% Gd; .09% Dy; trace Ta; Fe, Mg and Ca, not detected
Samarium	<.005% Fe; <.03% Ca; <.003% Mg; <.025% Dy; .007% Eu; <.02% Nd; .05% Gd

None of the metals used in the present work was analyzed for carbon, nitrogen and oxygen content. Typical analyses of other samples of gadolinium, terbium and samarium made by the same processes as referred to above revealed the carbon and nitrogen content of gadolinium and terbium to be between 110 and 150 p.p.m. Although no oxygen analyses were available for any of the metals, the oxygen content of samarium is expected to be less than 50 p.p.m. because a distillation process was used in its preparation. However, the oxygen content of gadolinium and terbium would be expected to approach that of yttrium since the same process was used in their preparations. Typical oxygen analyses of yttrium samples were available and ran about 2000 p.p.m. of oxygen.

Shavings were taken from the surface of the gadolinium after the metal was cast. The terbium and samarium samples were machined into samples of suitable shape and size.

Apparatus

Cryostat and related equipment

The cryostat and related equipment consisted essentially of a double dewar system, a vacuum system and the sample coils, which have previously been described (5). The setup was as follows. The sample coils were wrapped around a glass tube. This tube made a vacuum seal to a brass plate which in turn made a vacuum seal with the inner dewar. Another glass tube which contained the sample was introduced into the coil support tube through a vacuum coupling which allowed the sample to be translated in and out of the coils. The inner dewar was suspended in the outer dewar and the system between the sample tube and coil support tube was connected to a high vacuum line.

Sample compartment

The sample compartment consisted of a 21 mm pyrex tube which contained a cylindrically-shaped heater shell which rested at the bottom of the tube. The heater shell housed the sample or, in the case of gadolinium and terbium, the sample container which held the sample. Also, suspended within the

tube immediately above the heater shell was a cylinder of styrofoam around which were wrapped the leads from thermocouples placed in and above the sample and the heater leads.

The sample, after having been fitted into its container, was placed in the heater shell with cylindrical pieces of styrofoam on either side of it in order to locate the sample at the center of the shell (Figure 2). A thermocouple was inserted into a small opening in the center of the sample, wrapped several times around a groove in the sample holder and brought up through the piece of styrofoam immediately above it to a bakelite ring. Here another thermocouple junction was made so as to have a thermocouple above the sample as well as at its center. The thermocouple wires were wound around the ring and held in place with G. E. adhesive No. 7031. The three leads from the two thermocouples were then brought through another piece of styrofoam and out of the top of the heater shell. Both ends of the heater shell were plugged with pieces of bakelite. The top piece contained a groove to allow passage of the thermocouple wires.

The heater shell was made of a sheet of graph paper, .0033 inch thick and was 18 centimeters long. The paper was glued so as to form a hollow right circular cylinder, 7/8 inch i.d. It was then wound with a heater consisting of a non-insulated No. 40 B. & S. Be-Cu wire and a No. 32 B. & S. Formvar insulated copper wire. The two constituted a non-

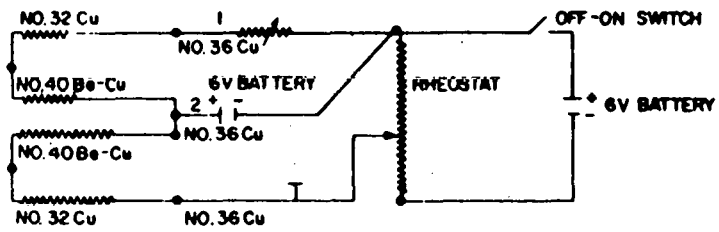


Figure 1. Heater circuit

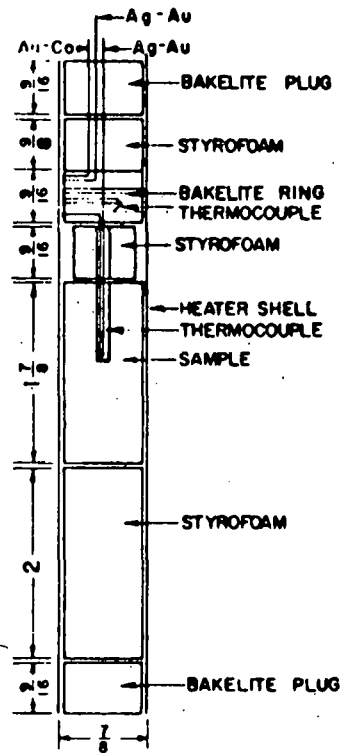


Figure 2. Heater shell

inductive, non-paramagnetic pair. The wires were held to the paper with G. E. adhesive. Two such heaters were wound on the shell. One extended the entire length of the shell and had a resistance of 124 ohms. The other was wound around the top one-third of the shell and had a resistance of 24 ohms. No. 36 B. & S. Cu wire was used to bring leads from each of the two No. 32 Cu wires and from the Be-Cu wire junction. The arrangement is shown in Figure 1.

The thermocouples were made of No. 30 B. & S. gold-cobalt and gold-silver enameled wire and contained 2% cobalt and .37% silver, respectively. They were used to measure temperatures from 4°K to 310°K. The thermocouple placed at the center of the sample was used to follow the sample temperature, while the thermocouple above the sample was used as a check on temperature equilibrium between the sample and sample container. The thermocouple wire was obtained from the Sigmund Cohn Corporation of Mt. Vernon, N. Y. The calibration of the thermocouple wire and the use of these calibrations for determining temperatures have been described (5). The amount of cobalt contained in the thermocouple wire was found to be small enough so as not to cause any significant error in our results (5). All thermocouple junctions were made with silver solder because lead-tin solder exhibits a superconducting transition with associated permeability change at helium temperatures.

All leads from the heaters and thermocouples were wrapped around a cylindrically shaped piece of styrofoam, 19 inches in length and $5/8$ inch in diameter, several times to increase the path length between the sample and the point at which the leads entered the sample compartment at room temperature. The heater shell containing the sample was fitted into the bottom of a pyrex tube, long enough so adjustments could be made to center the sample in the coils. The leads were brought up through a tee, which made a vacuum seal to the glass tube by means of a one-inch vacuum coupling, and then out of the sample compartment. At this point, the heater leads were soldered to heavier leads which were connected as shown in the heater circuit (Figure 1). The batteries were 6 volt Willard D-D-3 cells which supplied sufficient power over the entire temperature range. Referring to Figure 2, lead No. 2 is from the Be-Cu junction, lead No. 1 is from the 24-ohm heater and lead T is from the 124-ohm heater. The rheostat was used to control the heater current entirely except at higher temperatures when the thermocouple above the sample became cooler than the one in the sample. Only in this case was the lead No. 1 connected. This allowed for additional heat input at the top of the heater shell. The heater could not be turned off entirely unless the on-off switch was on off and the No. 2 lead was disconnected.

The thermocouple leads extended to an ice bath where the

junctions were made with copper wires. The three copper leads were brought from the ice bath and connected to two ends of a double pole double throw switch. The lead from the gold-cobalt wire was used for both thermocouples. The center taps of the switch were connected to a Rubicon, Type B potentiometer, Catalog No. 2780, used in conjunction with a Leeds and Northrup galvanometer, Catalog No. 2430A.

The mutual inductance bridge

The mutual inductance bridge used for all measurements was designed by L. D. Jennings and the details of such a design have been described (7). The use of this bridge for susceptibility work has also been described (5). Hence, only a brief summary will be given here. The circuit primary consisted of an oscillator in series with a power amplifier, the bridge primary, the sample primary and the external variable primary. The secondary half of the circuit consisted of the bridge secondary in series with the sample secondary, the transformer and external variable secondary. The signal from the transformer was amplified by means of a 33-cycle narrow band selective amplifier and was observed on an oscilloscope which was used as a null detector.

The dewar coils surrounding the sample were wound as an astatic pair so that the net mutual inductance in the absence of a sample was minimized. This net mutual inductance was

compensated for by adjusting the external variable balancing inductor. The real and imaginary parts of the mutual inductance were then balanced by the use of the standard inductors and the resistive network. Through the use of an external sync on the oscilloscope the magnitude and sign of both the real and imaginary parts of the mutual inductance could be readily identified. The mutual inductance range of the bridge was 2×10^{-10} to 6.53×10^{-5} henrys.

EXPERIMENTAL PROCEDURE

Preparation of Samples

To prepare the gadolinium sample, 0.1302 grams of gadolinium crystals about 0.5 mm on edge were uniformly distributed in 2.637 grams of softened bee's wax. This distribution was obtained by slowly adding the crystals to the wax while kneading the mixture at room temperature. The wax which contained the crystals was shaped into a spheroid to fit into a plexiglass sample container. The container consisted of two halves which fit together to form a cylinder with a spheroidal cavity having its major axis parallel to the cylinder axis. The cylinder was $7/8$ inch in diameter and fit snugly into the heater shell. It had grooves in which the thermocouple was wound after being inserted into the center of the sample. After the sample was placed in the sample container, the two halves of the container were fastened together with plexiglass cement.

The terbium sample was machined into a right circular cylinder and weighed 0.5280 grams. It was 0.072 inch in diameter and 1 inch long. It was fitted into a bakelite container which in turn fit snugly into the heater shell. The container was fitted with a lid which had a small opening through which the thermocouple passed. The thermocouple was simply wound around the terbium sample several times and

brought through the small opening in the lid.

The samarium sample was machined roughly into a cylinder to fit directly into the heater shell without being placed in a container. The sample weighed 59.345 grams. A large sample was necessary since the magnetic moment of samarium is relatively small. A small hole was drilled down into the center of the sample into which the thermocouple was fitted. The thermocouple was then wound around the sample lengthwise. The maximum diameter of the sample was $7/8$ inch and its length was $1\ 7/8$ inches.

Procedure for Taking Data

The sample was placed into its container and then centered longitudinally in the heater shell. The heater shell and attached leads were placed into a long Pyrex tube which fit into the dewar system and sample inductance coils through a vacuum coupling. The sample compartment was then pumped out to avoid any air oxidation of the sample, and filled with helium gas for better thermal contact between sample and heater. The inner system was then evacuated, using both the forepump and diffusion pump. The vacuum chamber of the inner dewar was also pumped out and flushed several times with dry nitrogen if it was suspected that helium had diffused into it. Once the system was evacuated, the sample was cooled down to 78°K with liquid nitrogen in the outer dewar. For runs on

gadolinium and terbium, liquid nitrogen was also placed in the inner dewar since the temperature range above 78°K was the one of interest. In the case of samarium, only the outer dewar was filled with liquid nitrogen and once the sample had cooled to the boiling point of liquid nitrogen, liquid helium was transferred into the inner dewar. Helium exchange gas was admitted into the inner system immediately after filling the dewars in order to cool the sample. Using liquid helium, a temperature of 4°K could be reached. When the desired temperature was reached, the helium exchange gas was pumped out of the inner system and the sample was then ready for measurement.

Before any measurements of mutual inductance could be made, however, the mutual inductance bridge first had to be balanced. Because the signal on the scope would be saturated, the gain on the amplifier had to be turned almost completely down and a balancing inductor used to unsaturate the signal. Once an unsaturated signal was obtained, the gain was slowly turned up as both the resistive and inductive components of the signal, which were 90° out of phase with one another, were balanced. The inductance switches on the bridge were varied in order to balance the inductive component of the signal and the resistance set-up was used to balance the resistive component. The circuit equations involved in the balancing of the bridge have been described in detail (5).

When the bridge was balanced, the position of the sample was then checked in order to make sure it was centered in the sample coils. This checking was done by translating the pyrex tube, containing the sample, with respect to the coils and noting the change in the off-balance signal to the oscilloscope from the bridge circuit. Whether or not the sample was centered was obvious from the change in the signal with respect to translation of the sample. The tube holding the sample was then clamped so that it could move no lower than the center position in the coils.

Once the bridge was balanced and the sample was centered, data which consisted of bridge inductive and resistive readings, and thermocouple readings were recorded. First an "in" reading, with the sample in the coils, was taken. Then the tube containing the sample was translated out of the coils and an "out" reading was taken, with the sample out of the coils. The tube was then lowered back to its original position and another "in" reading was taken. The thermocouple readings at the time of both "in" readings were recorded. These readings were usually the same unless the sample was kept out of the immediate vicinity of the helium bath long enough to warm. This warming only happened at very low temperatures. The sample was then heated slowly enough to obtain the necessary data in the particular temperature range in question. In the region below 20°K this meant a point

every 0.5° and between 20° and 30° K, a point every degree. From 30° up to 77° K, a point every four or five degrees was sufficient. Above 77° K a point was taken only every 10 degrees. Thermocouple readings and mutual inductance readings were recorded for every point. The bridge resistive readings were recorded about every four points. The "out" readings were checked often enough to be assured that their variation would involve an error of less than .1% in ΔM which is the difference between an "in" reading and an "out" inductance reading.

In order to take an "out" reading, the amount of heat which was being supplied to the sample was decreased until the temperature of the sample became constant. In the case of samarium this was not necessary since the sample had to be heated very slowly due to its large size. Data were taken on samarium at about one degree per 10 minutes as compared to points taken on terbium or gadolinium at about 10 degrees per four minutes.

Heat was supplied through the use of the hester circuit described under "Sample compartment". A check was kept on the amount of heat supplied to the sample, through the use of a voltmeter parallel with the heater. This check made it easy to adjust the heat for future runs.

Two kinds of runs were made. One, which will be referred to as a "heating run", was made by taking data as the sample

was heated to higher temperatures. The other will be referred to as a "cooling run" and was made by taking data as the sample was cooled. The number and kind of runs depended on the particular sample. In the case of gadolinium, only heating runs were made since there were no anomalies which were studied for hysteresis. Only the shape of the mutual inductance curve was of interest. Special attention was given to data taken in the region of 200°K where there was a maximum in the mutual inductance curve.

Terbium and samarium were both examined for hysteresis effects in the temperature ranges of 220°K and 15°K , respectively. For terbium, several heating runs and several cooling runs were made. Some heating runs were made by first cooling the sample to 78°K and allowing it to stand undisturbed overnight before taking data. Other heating runs were made by first cooling the sample to various points above 78°K in the range fairly close to the peak, and then taking heating points immediately.

Cooling runs were made by cooling down from room temperature, by cooling from various points above the peak, and by cooling from the same temperature above the peak to test for time dependence. The test for time dependence of the ΔM versus T curve for terbium was made as follows. Duplicate runs were made by heating the sample from a temperature below the peak to the same temperature above the peak and allowing

it to stand there for a few hours in one case and overnight in the other case. Also, runs were made by cooling the sample down to several temperatures below the peak and above 150°K and allowing the sample to stand for different lengths of time while the temperature was kept as nearly constant as possible. The longest length of time was 24 hours.

Samarium presented a problem in that the sample was so large that a very slow heating rate had to be used to obtain temperature equilibrium in the sample. Early data taken on this sample were irreproducible and it was concluded that this irreproducibility was due to the fast heating rate used since it was independent of the thermal history of the sample. The data taken at very slow heating rates were reproducible for a given thermal history and only these are included in Figure 6. Several heating runs were made by first cooling to various points below the peak and heating. Cooling runs were also made. This sample was also examined in the region of 105°K where a second peak occurred in the heat capacity curve (8). Runs were made in this region using both a liquid nitrogen bath and a liquid helium bath.

The accuracy of the thermocouples was checked to determine to within what limits the absolute value of any temperature was known. This was done by putting carbon disulfide into a bakelite container which was fitted into the apparatus. The carbon disulfide was then solidified and a plot of EMF

versus T was made of data taken through the melting point. Data obtained from this material proved very reproducible and a melting point of -112°C was obtained. The reported value was -111°C . It was concluded that the absolute value of a temperature was known to within a degree. This meant that the mutual inductance curve might be shifted one degree in one direction or the other, not that points were randomly in error by a degree in any direction.

RESULTS AND DISCUSSION

The paramagnetic properties exhibited by the rare earths and their salts arise from the incomplete subshell of 4f electrons which is present in the lanthanide series. Because of the high temperature free ion value of the magnetic moment in the rare earths, these 4f electrons are usually not considered to be conduction electrons. The screening effect, which is present in the pure metal as well as the salts, of the two complete subshells of higher principle quantum number (5s and 5p) should enable the atoms to behave as free ions except in the low temperature region where interaction between neighboring ions becomes important. It is this region with which this work is concerned.

The results of present work are discussed in terms of ΔM , the change in mutual inductance due to the presence of the sample, rather than magnetic susceptibility, assuming that the susceptibility goes as ΔM above the highest magnetic transition. The movement of domain walls becomes important below the Curie point but just how much this contributes to these measurements is not known. Because the exact contribution of the magnetic moment to ΔM , below the Curie point, is not known, a calculation of the absolute susceptibility below the Curie point is irrelevant here.

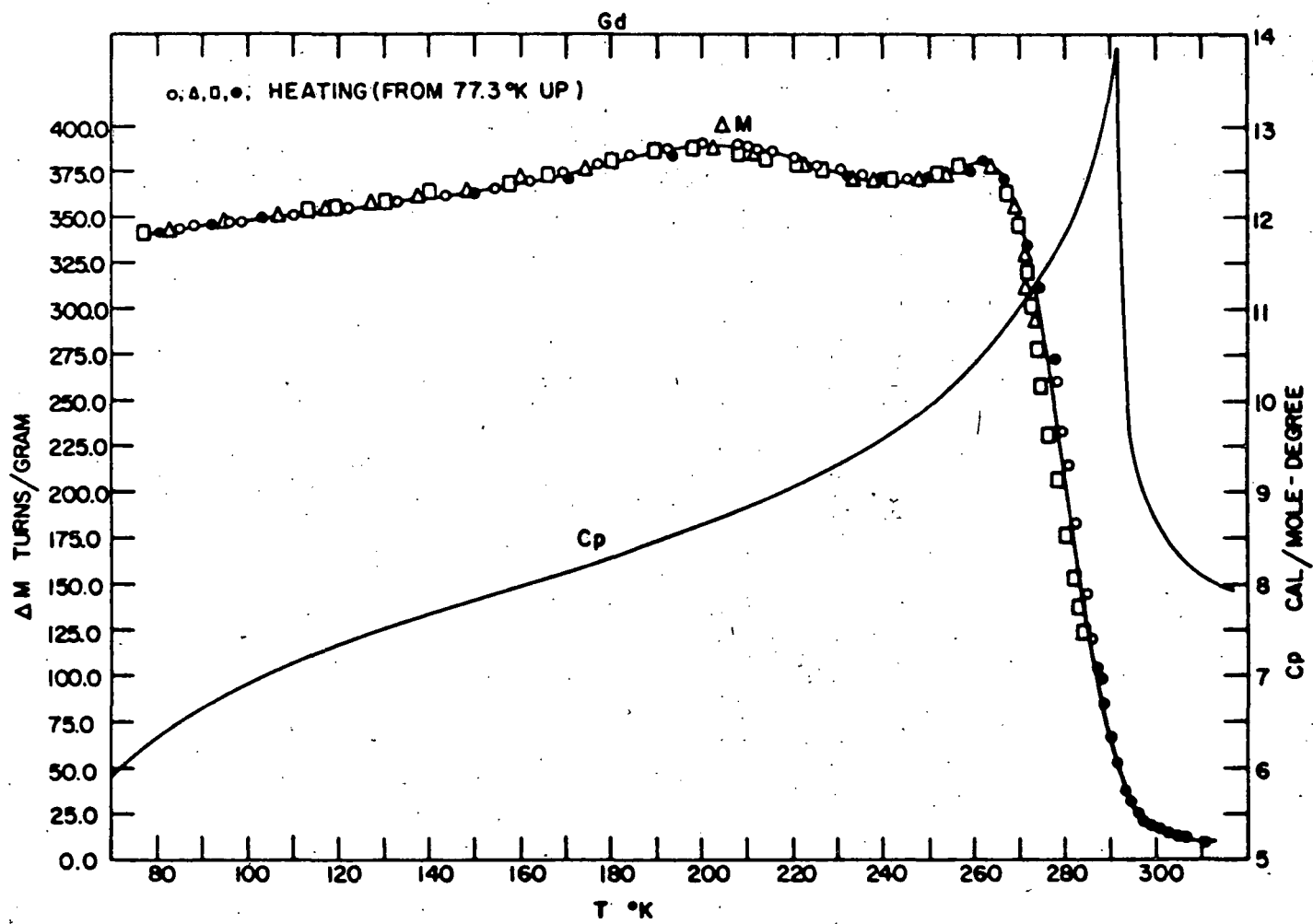
Gadolinium

The present magnetic work done on gadolinium has been to determine the shape of the curve of ΔM versus T from 78°K to 310°K in order to get an idea of its behavior in a region where the magnetic properties of the metal are known. Elliot, et al. (4) have made measurements over the temperature range of 20° to 250°K and have found gadolinium to have a paramagnetic Curie point of 289°K . They also reported no thermal hysteresis within 0.1° at the Curie point. Trombe (18) also reported a value of approximately 289°K for the Curie point. Klemm and Bommer (11) have reported an approximate Curie point of 300°K for gadolinium and a value of χ_{at} at 418°K of 64.5×10^{-3} . Kriessman and McGuire (12) have also studied the magnetic properties of gadolinium above 400°C and found that it obeyed the Curie-Weiss law $\chi_M = 8.21/(T - 298)$.

Griffel, et al. (6) observed an enhanced heat capacity, associated with the ferromagnetic transition, with a maximum at 291.7°K .

The curve of ΔM versus T , which represents the present work done on gadolinium, is shown in Figure 3. For comparison, the heat capacity curve has also been included in the figure. Above 70°K , the ΔM curve rises slightly as the temperature is increased and reaches a maximum at 202°K . It then decreases slightly to a minimum at 242°K where it begins to rise again. Another maximum is reached at 262°K and the curve

Figure 3. Change in mutual inductance versus temperature of gadolinium; specific heat versus temperature of gadolinium



then drops sharply until the temperature of 295°K is reached. Here it begins to level off to a straight line. A plot of $1/\Delta M$ versus T was made of data taken from 290° to 310°K . This plot (Figure 4), when extrapolated to a value of zero for $1/\Delta M$, yields a paramagnetic Curie temperature of 284.2°K . However, this plot of $1/\Delta M$ versus T is not linear. In order to obtain a more exact value of the paramagnetic Curie point it would be necessary to extend the temperature range above 310°K to the region of true paramagnetism. An extrapolation of the ΔM versus T curve in the region of the sharp rise, 270 - 290°K , to $\Delta M = 0$ yields a temperature of $292.5 \pm 1.5^{\circ}\text{K}$ which agrees more closely with the temperature at which the maximum occurs in the specific heat curve. It might be noted here that some discrepancy in the Curie point determination could arise from inhomogeneity of the sample. Behrendt, et al. (1) found a difference of 20° in Curie points of dysprosium, depending on whether the crystal axis was perpendicular or parallel to the field. The measurements of ΔM versus T on gadolinium were made on "as cast" samples, and it is possible that a preferred orientation existed in the sample, even though it was in the form of small particles embedded in wax.

Terbium

The magnetic properties of terbium have been studied by Klemm and Bommer (11) and by Thoburn, et al. (17) in fields of

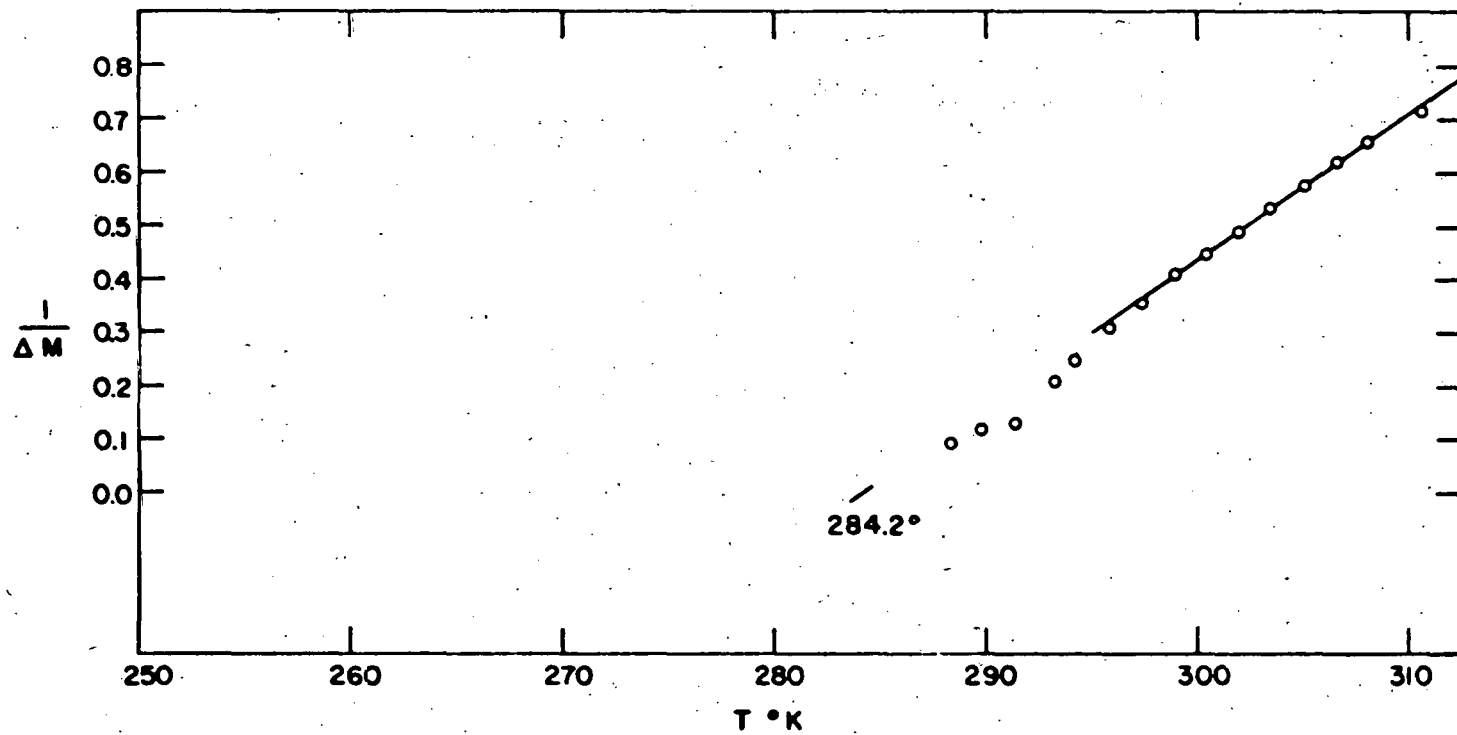
50 to 18,000 oe. The present work on terbium consisted of measurements in fields of about 2 oe.

Klemm and Bommer reported terbium to obey the Curie-Weiss law $\chi_{at} = 10.1/(T - 205)$ and obtained an atomic susceptibility at room temperature of 115×10^{-3} . Thoburn, et al. have measured the metal over the temperature range 4°K to 375°K and reported a paramagnetic Curie point of 237°K . Their measurements also indicated an order-disorder transition at approximately 230°K in fields of 50 to 800 oe and weakly bound antiferromagnetic ordering for temperatures between 218° and 230°K . The metal became ferromagnetic below 218°K . The antiferromagnetic ordering was found to disappear in fields above 200 oe.

Colvin (3) has made measurements of the resistivity of terbium. A plot of resistivity versus T showed the curve to change sharply in slope at 229°K and to increase only slightly in slope with increasing temperature at 219°K . Born (2) also reported a change in slope of his curve of thermoelectric power versus T at 232°K but detected no transition near 219°K .

Jennings, et al. (9) reported an anomaly in their specific heat versus temperature curve at 227.7°K , which showed up as a sharp peak, and also an anomalous region near 220°K which showed up as a slight bump in the curve. The heat capacity in the region of 220°K was found to depend upon the thermal history of the sample.

Figure 4. Reciprocal of change in mutual inductance
versus temperature of gadolinium



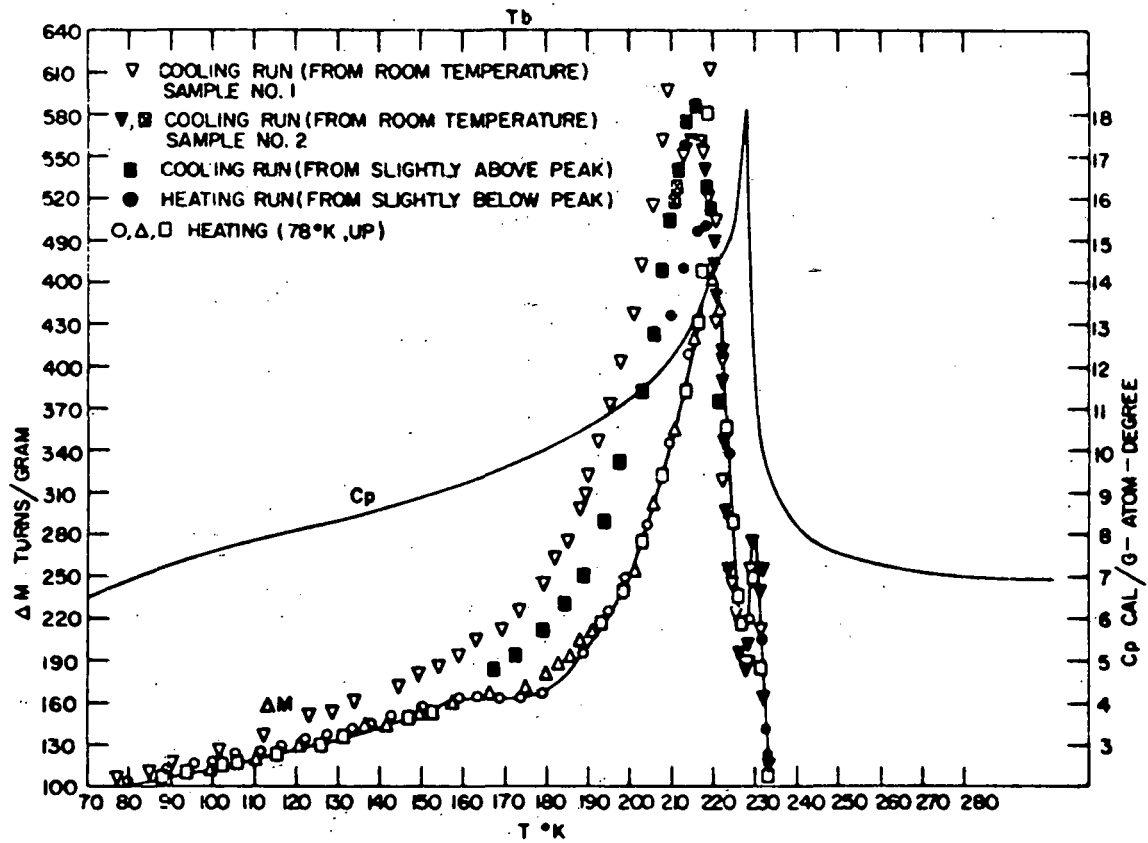
It was this region around 220°K that was thoroughly examined in the present work although measurements extended the whole temperature range from 78° to 235°K . Two terbium samples were used. The original sample, which will be referred to as sample No. 1, was too large to obtain points at the top of the peak when cooling from room temperature since the mutual inductance exceeded the maximum mutual inductance value of the bridge. One run, cooling from room temperature, was made on sample No. 1 and is represented by the inverted triangles in Figure 5. Sample No. 1 was cut in half and one half was sample No. 2. The reproducibility of data taken as the sample was cooled from room temperature was confirmed by making two cooling runs on sample No. 2. These runs are represented by the inverted blackened triangles and the squares with x's. Data from the above mentioned three runs, when normalized to change in mutual inductance per gram of sample, do not fall on the same curve below 220°K . Whether this is due to hysteresis, different preferred orientation in the two halves of the sample or additional strain due to machining, is not known. No heating runs were made on sample No. 2. The curve of ΔM versus T shown in Figure 5 reveals two peaks; one with a maximum at 219.5°K and the other at 229.4°K . The large peak in the mutual inductance curve corresponds to the small bump in the specific heat curve, also shown in the figure, and the small one to the sharp peak

in the specific heat curve. The terbium sample showed hysteresis in the region of 219°K . Data taken while heating the sample showed a maximum mutual inductance at 219.5°K and data taken while cooling showed a maximum at 215.7°K . This maximum at 215.7°K always occurred at the same temperature regardless of the treatment of the sample before cooling even though the ΔM values did not fall on the same curve unless the sample was cooled all the way from room temperature.

The general trend followed by the cooling curve was as follows. The cooling data fell on the heating curve as the sample was cooled over the peak at 229°K . When the minimum at 227°K was reached, the cooling data fell below the heating curve. After going through the minimum, the points fell about one degree to the left of the heating curve, rose above the heating curve as the sample was cooled past 220°K to a maximum at 215.7°K . As the temperature was further decreased the cooling curve slowly approached the heating curve until the two coincided at 78°K .

The original heating curve was reproduced only if the sample was cooled down to 78°K and allowed to stand for at least eight hours. Otherwise, varying curves would be obtained ranging anywhere between the original heating curve and the cooling curve representing data taken as the sample was cooled from room temperature. The sample was also found to exhibit time-dependence in the region of the peak at

Figure 5. Change in mutual inductance versus temperature of terbium; specific heat versus temperature of terbium



220°K.

An extrapolation of the ΔM versus T curve above 230°K to $\Delta M = 0$ gave a value for the Curie point of 235.6°K.

Samarium

Lock (14) has assumed from his work on samarium that it becomes anti-ferromagnetic below 14.8°K where he has found a maximum in the susceptibility. The curve of susceptibility versus temperature dropped sharply below 14.8°K and started to rise again below 7°K. Lock also reported a kink in the curve around 105°K corresponding to a drop in the susceptibility of about 5%. From 150°K up to room temperature he found that the susceptibility varied no more than 2% and followed no form of the Curie-Weiss law. The value given by Lock for $10^3 \chi_{\max}$ per gram atom at 14.8°K was 1.82.

Heat capacity measurements on samarium revealed two peaks in the curve of C_p versus T , one at 105°K (8) and the other at 13.8°K (15). Although the peak at 105°K contained more entropy than did the lower temperature peak, only a slight indication of this high temperature anomaly was seen in the susceptibility measurements of Lock and in the work presented here no anomaly of significant size was found around 105°K. Resistivity measurements, however, done by Curry (2) showed a change of slope in the resistivity versus temperature curve at 105°K which was temperature dependent, indicating that some

magnetic ordering does occur.

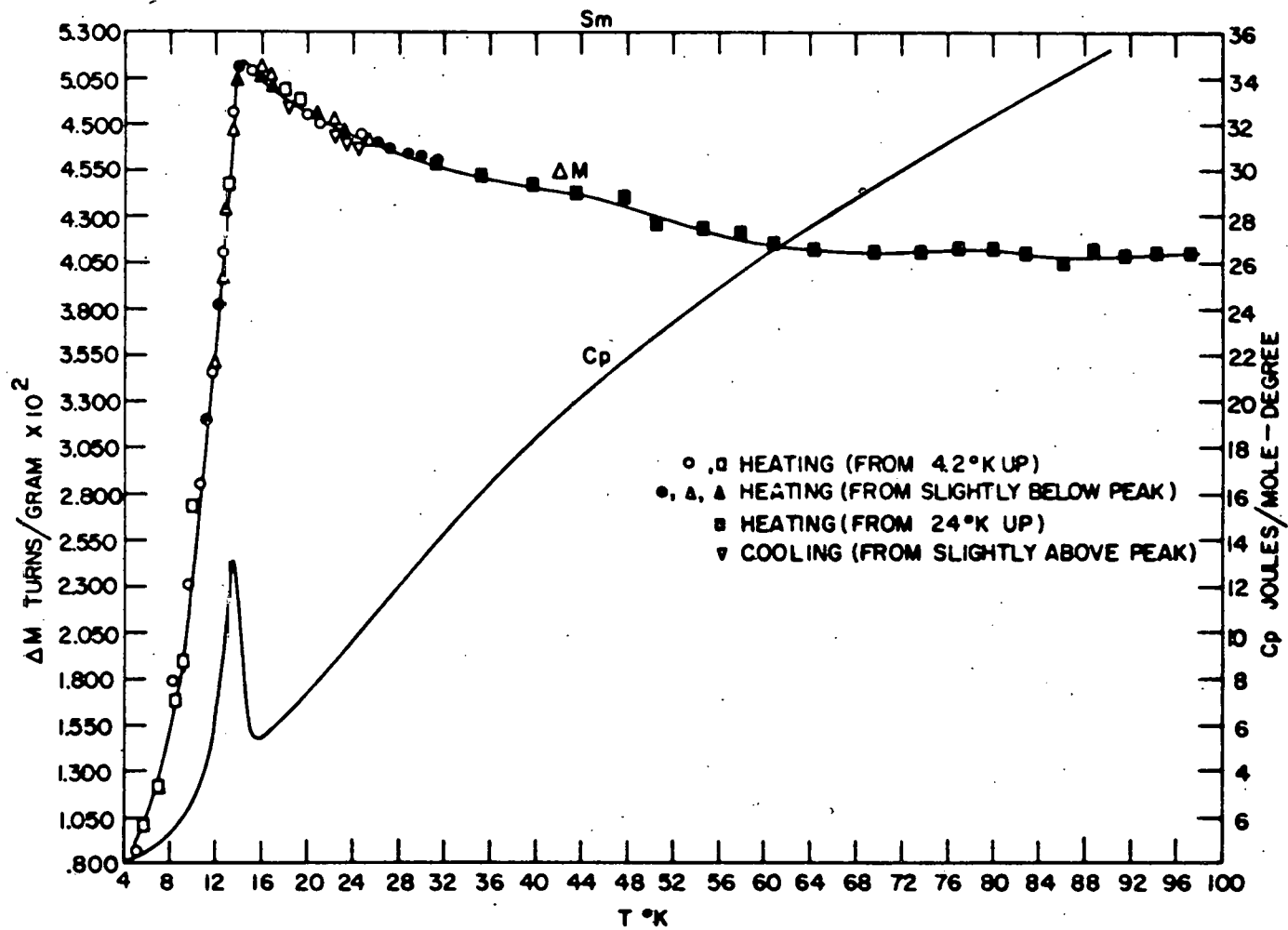
Heat capacity measurements made in this Laboratory (8) showed a rise in the specific heat curve between 14.4° and 12.7°K , but since measurements could not be made below 12.7°K the maximum could not be seen. Roberts (15), however, reported a maximum in her heat capacity versus temperature curve at 13.8°K . The reason for the difference in the two curves was not known.

Zero field mutual inductance measurements were made on samarium down to 4.2°K which, after careful examination, proved that either the samarium sample showed no hysteresis or that it could not be detected by this method. In the case of terbium, however, hysteresis effects were clearly seen by the mutual inductance method and recent inductive measurements made on thulium* show this metal to exhibit hysteresis in the hydrogen range of temperature. It is probable, therefore, that no hysteresis of the type observed in thulium and terbium exists in samarium in the region of 14.8°K .

The ΔM versus T curve and the heat capacity curve (Robert's data is plotted below 20°K) for samarium are shown in Figure 6. The maximum in the ΔM curve occurs at 14.9°K which closely agrees with data taken by Lock (14). This temperature is higher than that of the heat capacity maximum of

*Investigation was made in the Ames Laboratory.

Figure 6. Change in mutual inductance versus temperature of samarium; specific heat versus temperature of samarium



Roberts (15) by 1.1° and even still higher than that indicated in our heat capacity work (8). No increase in ΔM was found below 7°K to agree with the increase in χ as reported by Lock.

There appeared a bump in the ΔM versus T curve of samarium around 77°K which did not show up in all runs and therefore was not investigated thoroughly.

Born (2) reported only a barely discernible bump in his curve of thermoelectric power versus temperature at 105°K .

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APPENDIX

The tables which follow contain data in final form as plotted in the graphs on preceding pages. The temperature is given in $^{\circ}\text{K}$ and change in mutual inductance, denoted by ΔM , is given in turns per gram. One turn is equivalent to 2×10^{-8} henry.

Table 1. Change in mutual inductance of gadolinium

T °K	ΔM turns/gram	T °K	ΔM turns/gram	T °K	ΔM turns/gram
<u>Series 1</u>					
77.3	340.17	138.3	359.68	220.3	381.80
82.4	342.09	143.5	361.52	225.3	377.88
85.3	343.32	149.0	362.52	230.4	375.19
88.2	344.39	154.1	365.21	235.4	372.73
91.0	345.39	161.9	369.43	240.5	371.35
93.0	345.47	169.6	373.66	245.5	370.66
95.9	346.31	177.2	378.19		
98.7	347.16	183.9	383.18		
101.5	348.08	192.4	387.56		
104.3	348.93	200.0	389.86		
110.2	350.77	205.2	389.86		
114.8	352.15	207.4	389.40		
122.4	354.61	209.9	388.48		
127.7	356.45	212.4	387.10		
133.1	358.06	215.5	385.33		
<u>Series 2</u>					
77.3	340.71	184.9	381.49	269.5	35.62
81.0	341.78	189.9	384.03	271.7	319.12
86.8	343.40	195.0	385.87	273.0	301.61
92.5	345.16	197.5	386.56	274.5	278.19
102.3	348.31	203.8	386.33	275.8	258.06
107.9	349.85	206.4	385.56	277.3	232.41
113.3	351.69	208.9	384.33	278.8	207.30
118.7	353.38	213.9	381.72	280.8	174.88
124.0	354.92	221.5	376.73	282.3	152.30
129.3	356.45	226.1	374.27	283.3	137.63
134.7	358.14	231.1	372.27	284.3	123.96
139.9	359.99	236.2	370.97		
145.1	361.83	241.2	370.58		
150.3	363.90	246.8	371.51		
155.4	365.98	251.3	373.57		
160.6	368.36	255.6	376.57		
165.7	371.04	260.6	380.03		
170.9	373.66	263.2	379.03		
176.0	376.42	264.4	376.65		
179.8	378.73	266.9	365.82		

Table 1. (Continued)

T_{OK}	ΔM turns/gram	T_{OK}	ΔM turns/gram	T_{OK}	ΔM turns/gram
<u>Series 3</u>					
82.5	342.17	180.5	376.73	258.1	376.73
94.7	346.16	193.1	383.56	261.6	379.03
106.0	349.54	202.6	386.41	263.7	377.50
116.8	353.15	212.7	384.33	265.7	373.20
127.5	356.30	222.8	376.57	268.2	356.84
138.1	359.91	232.9	370.20	270.7	330.26
148.4	363.59	237.9	368.89	272.0	313.83
158.8	367.90	243.0	368.51	273.2	296.01
163.9	369.82	248.0	369.59		
174.2	375.04	253.1	372.50		
<u>Series 4</u>					
80.6	341.32	277.7	272.73	297.4	21.51
92.2	345.82	278.5	259.45	298.9	18.74
103.2	352.69	279.5	233.33	300.4	17.20
150.0	361.83	280.8	214.21	302.0	15.59
170.6	370.20	282.3	183.03	303.5	14.36
193.5	382.87	284.3	144.78	305.0	13.29
206.2	388.02	285.9	119.74	306.5	12.44
232.0	372.43	286.9	104.30	308.0	11.67
239.7	371.51	287.9	98.08	310.5	10.52
249.8	371.58	288.4	83.87		
258.9	373.73	289.9	66.36		
262.4	380.42	291.4	51.69		
266.7	371.20	293.2	36.79		
271.8	339.25	294.4	31.11		
275.7	311.29	295.9	25.27		

Table 2. Change in mutual inductance of terbium

T °K	ΔM turns/gram	T °K	ΔM turns/gram	T °K	ΔM turns/gram
<u>Series 1</u>					
77.3	102.63	127.6	136.91	179.0	166.34
79.5	103.88	133.8	141.34	184.1	181.15
83.5	108.35	137.9	144.75	189.0	194.69
89.2	109.92	143.1	149.83	194.1	220.83
94.8	113.63	148.3	154.50	199.1	248.67
100.4	117.42	150.8	156.74	204.2	286.76
106.0	121.23	159.0	162.72	209.4	344.18
111.4	126.04	163.7	163.65	214.2	408.14
116.7	128.90	168.8	163.12		
122.1	132.89	173.9	162.55		
<u>Series 2</u>					
77.3	98.29	152.1	152.27	228.3	218.48
82.0	101.53	157.3	156.44	229.0	251.09
84.9	103.24	184.1	177.93	229.5	277.21
87.7	105.00	192.8	213.39	229.8	275.94
93.4	108.43	197.9	241.57	230.3	245.89
101.8	113.73	202.9	275.11	231.3	183.06
104.6	115.36	207.9	321.17	233.3	107.33
110.1	119.32	213.0	382.42		
115.4	122.76	216.2	421.62		
120.7	126.36	219.2	466.26		
126.1	129.30	220.5	457.83		
131.4	133.88	223.2	356.19		
136.6	138.37	224.5	287.51		
141.8	142.57	225.7	236.07		
147.0	147.52	227.0	215.74		
<u>Series 3</u>					
209.8	435.67	226.3	238.88		
210.7	443.23	227.5	214.90		
213.0	469.63	228.3	212.91		
216.9	497.30	228.8	219.88		
218.2	498.53	230.8	219.88		
220.0	487.02	230.1	275.03		
221.2	454.35	230.8	257.23		
222.7	404.40	231.5	204.62		
224.0	337.44	232.8	141.66		
225.0	285.13	233.3	124.32		

Table 2. (Continued)

T °K	ΔM turns/gram	T °K	ΔM turns/gram	T °K	ΔM turns/gram
<u>Series 4</u>					
231.9	208.39	219.0	612.45	173.9	228.93
230.8	257.31	209.4	598.47	168.8	214.01
230.0	276.51	207.9	563.26	163.7	202.44
229.5	255.81	205.6	516.52	159.0	193.35
228.8	216.78	202.9	474.27	154.7	188.22
228.3	202.06	200.6	438.87	149.6	180.60
227.5	192.19	197.9	404.90	144.5	176.61
227.0	191.32	195.6	373.87	134.0	161.13
226.3	196.97	192.8	348.57	128.7	154.98
225.7	201.61	190.5	322.32	123.4	148.65
225.0	225.56	189.0	311.21	112.8	136.36
224.5	244.28	187.9	300.58	101.8	124.85
223.2	310.77	185.4	272.46	90.6	114.51
222.0	404.16	182.7	263.18	84.9	109.62
220.5	504.74	179.0	246.89	78.0	103.22
<u>Series 5</u>					
222.0	373.06	207.9	468.65		
220.3	459.12	205.6	422.95		
219.2	512.91	202.9	382.95		
217.7	566.81	197.9	323.57		
216.9	581.01	194.1	288.65		
215.7	584.25	189.0	253.74		
214.2	576.41	184.1	228.44		
213.0	560.03	179.0	208.42		
211.7	540.05	172.6	192.27		
210.7	517.13	167.5	182.29		
<u>Series 6</u>					
99.0	112.38	177.7	174.20	215.5	418.10
110.1	119.86	180.2	179.14	218.5	457.51
120.7	127.84	182.7	186.06	220.0	465.46
126.1	131.99	185.4	193.56	220.5	462.76
136.6	141.00	187.9	202.44	222.0	438.21
141.8	144.85	188.8	202.42		
149.6	152.08	190.5	210.94		
157.3	158.99	200.6	251.91		
166.2	164.92	205.6	302.08		
175.2	170.51	210.7	351.94		

Table 2. (Continued)

T °K	ΔM turns/gram	T °K	ΔM turns/gram	T °K	ΔM turns/gram
<u>Series 7</u>					
219.6	503.76	212.7	546.89		
218.7	529.12	211.9	542.28		
215.8	541.31	211.5	534.93		
217.2	559.46	211.0	528.91		
216.6	562.62	209.6	512.62		
215.8	563.30	209.2	504.84		
215.3	563.10				
214.8	561.90				
214.3	559.57				
213.3	552.75				
<u>Series 8</u>					
233.3	115.36	222.6	347.27	216.7	560.29
232.1	164.51	222.1	380.74	216.5	562.26
230.8	240.34	221.6	410.91	215.8	563.38
229.6	227.66	221.2	433.14	214.8	561.94
228.9	202.55	220.8	452.60	213.6	555.36
227.7	185.37	220.3	477.88	213.1	551.58
227.1	185.81	220.0	489.83	212.3	544.60
225.8	200.46	219.1	524.26	211.1	532.20
224.0	258.04	218.2	542.40		
223.3	297.88	217.5	554.19		

Table 3. Change in mutual inductance of samarium

T °K	ΔM turns/gram	T °K	ΔM turns/gram	T °K	ΔM turns/gram
<u>Series 1</u>					
5.16	.00863	16.1	.05075		
8.38	.01766	16.8	.05031		
9.75	.02305	17.5	.04991		
10.8	.02846	18.8	.04922		
11.8	.03456	20.1	.04841		
12.7	.04111	21.2	.04779		
13.6	.04866		.04681		
14.5	.05102		.04631		
14.9	.05109				
15.3	.05089				
<u>Series 2</u>					
5.67	.01009	14.9	.05124	21.2	.04833
7.00	.01212	15.3	.05109	22.4	.04787
8.50	.01673	15.7	.05094	23.5	.04730
9.13	.01892	16.5	.05067		
10.3	.02734	16.8	.05052		
11.3	.03180	17.5	.04993		
12.4	.03843	18.2	.04991		
13.2	.04470	18.8	.04949		
14.1	.05042	19.4	.04922		
14.5	.05117	20.1	.04895		
<u>Series 3</u>					
12.0	.03498	17.5	.05013		
12.7	.03960	18.8	.04951		
13.2	.04354	20.1	.04902		
13.6	.04752	21.2	.04854		
14.1	.04814	22.4	.04811		
14.5	.05099	23.5	.04757		
14.9	.05126				
15.3	.05122				
16.1	.05104				
16.8	.05052				

Table 3. (Continued)

T OK	ΔM turns/gram	T OK	ΔM turns/gram	T OK	ΔM turns/gram
<u>Series 4</u>					
11.3	.03200	18.8	.04942		
12.3	.03817	20.1	.04893		
13.2	.04782	21.8	.04821		
14.1	.05107	23.5	.04772		
14.5	.05124	24.9	.04735		
14.9	.05126	26.3	.04693		
15.3	.05104	27.3	.04659		
16.1	.05063	28.8	.04630		
16.5	.05045	30.0	.04605		
17.5	.05003	31.4	.04582		
<u>Series 5</u>					
26.5	.04681	18.5	.04898	14.1	.05075
24.6	.04674	17.5	.04961		
23.5	.04698	16.1	.05038		
22.4	.04743	15.3	.05060		
20.6	.04814	14.5	.05126		
<u>Series 6</u>					
13.9	.05023	17.1	.05003	22.1	.04797
14.5	.05111	17.9	.04969	23.3	.04758
14.9	.05106	18.5	.04939	24.4	.04728
15.3	.05106	19.8	.04888	25.5	.04696
16.1	.05055	20.9	.04843		
<u>Series 7</u>					
24.6	.04703	60.6	.04150	91.4	.04089
26.3	.04682	64.3	.04110	94.3	.04091
31.2	.04571	67.8	.04194	97.1	.04098
35.7	.04506	69.5	.04096		
39.7	.04453	73.7	.04140		
43.5	.04416	77.0	.04123		
47.4	.04383	80.0	.04110		
50.9	.04260	82.9	.04105		
54.4	.04219	85.7	.04063		
57.6	.04186	88.6	.04088		