Hall effect at low temperatures for rare earth metals

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HALF DECTECT AT LOW TEMPERATURES
FOR RARE EARTH MEALS

by

Clement J. Kevane

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of

doctor of philosophy

Major Subject: Physics

Approved:

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1953
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I. INTRODUCTION

The Hall effect is of fundamental importance in the study of metals because it gives information about the numbers and types of carriers of electrical current in a metal.

The Hall effect is the setting up of an electric field, $\overrightarrow{E}_H$, in a conductor through which a primary electric current, of density $\overrightarrow{J}$, is flowing in a magnetic field, $\overrightarrow{B}$. The Hall field, $\overrightarrow{E}_H$, is related to the primary current and magnetic field through the expression, $\overrightarrow{E}_H = R(\overrightarrow{J} \times \overrightarrow{B})$, where $R$ is called the Hall coefficient for the material of the conductor. This simple relation holds for non-magnetic materials but must be replaced by another expression when appreciable magnetisation exists in the conductor. The theory of electrical conduction leads to expressions for the Hall coefficient, $R$, and by determining the algebraic sign and magnitude of $R$, one obtains, in the framework of the theory, the desired information about the carriers.

The study of the Hall effect in rare earth metals is of interest because of the relations between the electronic configurations of the free atoms of these elements. In the lanthanum series of rare earth metals these configurations differ principally in the occupation of the 4f electronic energy states and not in the occupation of valence states, which are ordinarily supposed to be the ones which become of importance for electrical conduction in the condensed, or metallic, state. Study of the Hall effect in these rare earth metals should yield information about the conduction bands and how they are affected by the population of the 4f, or
inner, electronic energy states in the free atom.

With the availability of appreciable quantities of many of the lanthanum rare earth metals of high purity, it became possible to carry out an investigation of the Hall effect in some of them.

The range of temperatures below room temperature was of special interest principally because of previous investigations of other properties of metallic cerium at low temperatures. Electrical resistivity, magnetic susceptibility, crystal structure, and other properties show remarkable behavior in the temperature range near 100° K. and below. It has been suggested that this behavior is associated with a shift of an electron from a 4f state to a 5d state when the temperature is lowered below about 100° K. Since the Hall effect gives information about the numbers and types of carriers of electrical current, it was thought possible that a study of the Hall effect in the temperature range below room temperature might give direct evidence contradicting or supporting the hypothesis of a 4f→5d shift.

In order to facilitate the study of the Hall effect over a wide temperature range, the measurement method selected was an a.c. method in which the metal sample is placed in a steady magnetic field and an alternating primary current is supplied to the sample. The resulting Hall voltage is alternating with the same frequency as the primary current and can be amplified and measured by means of an a.c. amplifier. The principal advantage of the method is that no correction for the Ettingshausen and other thermal effects is necessary.

Two of the properties of these rare earth metals are such as to influence the results of Hall effect measurements and it was necessary to consider them in the interpretation of the results. The first of these is
allotropy. Several of the rare earth metals of the lanthanum series have
been reported to exist in either the face-centered cubic or hexagonal forms,
or in mixtures of the two. Since it is possible that the Hall effect
depends significantly on the crystal structure, it was attempted to deter-
mine the structure of each of these metals before and after each of various
heat treatments to which it was subjected. A companion sample of the same
metal was subjected simultaneously to the same heat treatment as the one
on which the Hall effect measurements were made. X-ray analyses were then
made of the companion sample to determine, if possible, what the structure
was before a heat treatment and what effect the heat treatment had on the
crystal structure.

The other property requiring special consideration is the magnetic
property. Some of the rare earth metals of this series have been reported
to be ferromagnetic with Curie temperatures below room temperature, and
all but lanthanum have been reported to be rather highly paramagnetic in
this temperature range. Since it has been found that magnetization in
other metals has a very strong influence on the Hall effect, special con-
sideration of the magnetic state is required in the interpretation of
results. Where magnetization is present the Hall effect does not give
directly the numbers and types of carriers involved in conduction, but it
is necessary to take account of the effect of magnetization before this
information can be obtained. No attempt was made to make measurements of
the magnitudes of the Hall coefficients below the Curie temperatures of
those rare earth metals becoming ferromagnetic since this requires a some-
what different technique, the magnetic saturation of the sample being
necessary.
The investigation of the Hall effect in polycrystalline, metallic lanthanum, cerium, praseodymium, neodymium, gadolinium, dysprosium and erbium was carried out in the temperature range 20° K. to 300° K. except for those which are known to be ferromagnetic. The ferromagnetics were studied quantitatively only above their Curie temperatures, in the regions where they are paramagnetic. The impurity content of each sample was determined spectrographically and structure studies were made of those known to exhibit allotropy.
II. REVIEW OF LITERATURE

Inasmuch as the literature concerned with the Hall effect is voluminous, this review is not intended to be exhaustive, but is, rather, intended to represent only the work done which relates most directly to this study of the rare earth metals. A review of the early work on the Hall effect may be found in a monograph by Campbell (1933) and more recent work is described by Weissner (1955).

The results of existing theories will be presented, typical work using the measurement method selected here will be cited, and other work on the Hall effect in metals having strong magnetic properties will be included. Finally, the work which has been done on other properties of rare earth metals which affect the interpretation of the results of the Hall effect measurements will be cited.

A. Hall Effect Theory

The free electron theory of the Hall effect as discussed, for instance, in Seitz (1940) leads to an expression for the Hall coefficient, E. The result of the theory is that the Hall coefficient is given by

\[ R = - \frac{1}{\text{Nea}} \]

where \( N \) is the number of atoms per unit volume in the metal, \( -e \) is the charge on the carriers, and \( n \) is the number of carriers per atom contributing to conduction.
The band theory, as in Seitz (1940), in which account is taken of the periodicity of the potential field in which electrons move in a crystal, gives a means for understanding how the Hall coefficient can be either positive or negative. If the conduction band of electronic energy states is nearly full, conduction will be by positive holes and the Hall coefficient will be positive. If the band is nearly empty, conduction will be by electrons and the Hall coefficient will be negative.

A two-band theory of the Hall effect by Sondheimer (1948) treats the case of conduction involving two overlapping bands, one of which is nearly full, and one of which is nearly empty. The nearly-full band gives a positive contribution to the Hall effect and the other gives a negative contribution. The expression for the Hall coefficient according to this theory is

\[ R = \frac{1}{Ne} \left[ \frac{n_2 - n_4 \mu_2^2 / \mu_1^2}{n_2 + n_4 \mu_2^2 / \mu_1^2} \right] \]

where \( e \) is the magnitude of the electronic charge, \( N \) is the number of atoms per unit volume, \( n_2 \) is the number of holes per atom in the nearly-full band, \( n_4 \) is the number of electrons per atom in the nearly-empty band, \( \mu_2 \) is the mobility of the holes, and \( \mu_4 \) is the mobility of the electrons. Mobility is defined by the relation, \( \nu = \mu E \), where \( \nu \) is the drift velocity of a carrier and \( E \) is the electric field in the metal.

Pugh, Rostoker and Schindler (1950) have used this theory to account for the observed Hall effect and magnetic properties in nickel. Gehlhoff, Justi, and Kohler (1950) have used it as a means of understanding the observed Hall effects in the transition metals of the fifth and sixth
periods. It may be useful in interpreting the results of Hall effect measurements in metals of the rare earth series where 5s and 5d states may well be important in the conduction process.

The one-band free electron theory predicts no temperature variation of the Hall coefficient. The two-band theory could account for a temperature variation if the mobility ratio, $\mu_d/\mu_n$, were considered to be temperature dependent. A temperature dependence in $n_d$ and $n_n$ could also account for it.

B. Measurement Method

Many techniques for measuring the Hall effect have been reported. Descriptions and discussions of a wide variety of methods may be found in Campbell (1923) and Weissner (1935).

The sample is usually in the form of a rectangular parallelepiped. Primary current, $I$, flows along the length of the sample which is placed with its shortest edge in the direction of a magnetic field, $B_0$, and the Hall voltage, $V_H$, is measured across the centers of the two longest edges (see Figure 5). For this arrangement the Hall coefficient is given by $R = \frac{V_H I}{n_0}$, where $t$ is the smallest dimension of the sample, $V_H$ is the Hall voltage, $I$ is the primary current, and $B_0$ is the magnetic field. Isemberg, Russell, and Greene (1943) have shown that, if the length of the sample is at least four times the width, no correction is necessary for the effect of the current connections at the ends of the sample.

The most common method of measuring the Hall effect has been the d.c. potentiometer method in which the sample is placed in a steady magnetic field, a direct current flows along its length, and the resulting d.c.
Hall voltage across the width of the sample is measured by means of a potentiometer. Thermoelectric and thermomagnetic effects are eliminated in this method by immersing the sample in a liquid, by ensuring that no Hall current flows, and by commuting the current and magnetic field.

Hall effect measurements on metals at low temperatures have been made by several workers using the d.c. potentiometer method with the metal samples immersed in low-boiling liquids. No reports have been made of measurements of the Hall effect in metals at low temperatures other than those attained by immersing directly in liquids.

Another method of measuring the Hall effect is an a.c. method in which the same type sample is used but which differs in that the primary current is alternating. The magnetic field is steady and the resulting Hall voltage is alternating with the frequency of the primary current and can easily be amplified and measured. The advantage of this method is that it eliminates the necessity of correcting for thermoelectric and thermomagnetic effects.

Smith (1912), in studying the effect of varying the frequency of the primary current on the measured Hall effect in bismuth, found that this a.c. method gave the same result as the d.c. potentiometer method for frequencies up to 120,000 c.p.s. More recent work has been done by Levertun and Hakker (1950) using an a.c. method to study the Hall effect in thin films of antimony. They used alternating primary currents of 210 c.p.s. Donoghue and Etherly (1951) used an a.c. potentiometer method in studying the Hall effect in the graphitization of carbon. They used alternating current of 100 c.p.s.
C. Magnetic Effects

It has been proposed by Pugh (1930) that the Hall effect in ferromagnetics may be expressed by the relation

\[ V_H = \frac{I}{t} \rho_0 (H + 4\pi M) \]

where \( I \) = primary current, \( t \) = sample thickness, \( M \) = magnetising field, \( V_H \) = Hall voltage, \( \rho \) = intensity of magnetisation, \( \rho_0 \) = ordinary Hall coefficient, and \( \alpha \) is a parameter indicating the effectiveness of magnetic moment in deflecting conduction particles. The ordinary coefficient, \( \rho_0 \), is the one associated with carrier density in the electron theory of the Hall effect.

\( \rho_0 \) and \( \alpha \) have been determined at room temperature in the case of nickel by Pugh, Rootker and Schindler (1930) and it has been found by them that \( 4\pi \alpha \) is of the order of magnitude of 150 at that temperature. From this result, one can see that when magnetization is present in a metal, it may have a strong influence on the Hall effect and special methods are required to separate the ordinary and extraordinary effects. Usually, this is done in ferromagnetics by studying the Hall voltage as a function of magnetic field beyond magnetic saturation.

In a paramagnetic substance, the magnetic susceptibility is not field dependent and intensity of magnetization, \( M \), is given by \( M = \chi H \) where \( H \) is the magnetizing field, and \( \chi \) the paramagnetic susceptibility. In the usual experimental arrangement for making Hall effect measurements, the magnetizing field, \( H \), is given by \( H = H_0 - 4\pi M \) where \( H_0 \) is the external field and \( M \) is the intensity of magnetization. In this case one gets for
the Hall voltage,

\[ V_H = \frac{I}{t} B_o H_o \left[ \frac{\mu_0 \tau a X}{1 + 4 \pi X} \right], \]

If a Curie law of paramagnetism is obeyed, then \( X(T-\Theta) = C \) and

\[ \frac{V_H}{I H_o} = B_o \left[ \frac{T-\Theta + 4 \pi C}{T-\Theta + 4 \pi C} \right], \]

where \( \Theta \) is the paramagnetic Curie temperature, \( T \) is the temperature, and \( C \) is the Curie constant.

If one considered \( B_o \) and \( a \) to be independent of temperature, one would be able to determine them by fitting this function to the experimental plot of \( \frac{V_H}{I H_o} \) against temperature. However, it has been found by Pugh, Rostoker and Schindler (1950) in analyzing older data of Smith, that \( a \) is strongly temperature dependent in nickel. In the paramagnetic region they concluded that \( a \) had fallen to zero when the nickel sample was 150° C. above the Curie temperature.

This work indicates that the effect of magnetization may be of great importance in the Hall effect in paramagnetic materials and especially at low temperatures where the susceptibilities can become quite large.

D. Lanthanum

1. Crystal structure

Lanthanum metal has been reported to exist in two allotropic forms, the face-centered cubic and hexagonal closest packed, or in mixtures of the two. The results obtained by various workers indicate that the structure
is influenced by heat treatment and by impurities. Zintl and Neumayr (1933) studied the structure of lanthanum before and after annealing at 350° C. They found the hexagonal structure before the annealing and found the face-centered cubic structure after annealing. The metal used by Zintl and Neumayr was made by an electrolytic method and the purity was 99.9 per cent, the principal impurities being silicon and aluminum.

Kleemann and Bommer (1937) found only the face-centered cubic structure in lanthanum metal which had been prepared by the reduction of the chloride with liquid alkali. Ziegler (1949) found the hexagonal structure before annealing 96 hours at 350° C., and found the face-centered cubic structure after annealing. The lanthanum used by him was 99 per cent pure.

2. Magnetic properties

The magnetic properties of metallic lanthanum were studied by Kleemann and Bommer (1937) and by Trombe (1937). Kleemann and Bommer worked with an inseparable mixture of metal and rare earth chloride, while Trombe used only metallic lanthanum.

Trombe carried out measurements of the magnetic susceptibility in the temperature region 300° K. to 90° K. He found that the Curie law of paramagnetism was not closely obeyed, the \((x)^{-1}\)-temperature plot being concave downward. The magnetic susceptibility per gram, \(x\), decreased from 2.897 \(x 10^{-6}\) at 88.5° K. to 1.183 \(x 10^{-6}\) at 289.7° K.
which had been slow-cooled from 900°C to room temperature did not show
the parameter was 6 per cent wetter than the normal one at 700°. Certain
parameters, but which had a reduced intensity parameter, the reduced Ie-

certain structures at 700°, which were still face-centered cubic, at room
which had been quenched from 900°C to room temperature exhibited a new
antiparallelism of almost 100% of 37°O showed these crystals
other parameters of certain other ammonium benzenes near 100°C.

The certain 6 hour at 900°C. The certain to need was 6.6% per cent rate.
Zeller (1949) found only face-centered cubic before and after anneal-
face-centered cubic and hexagonal structures at 99.9 per cent rate. action
Gansnitz and Snow (1979) found both
and show that for room temperature at room temperature for total
both the face-centered cubic structures at 100°C near 99.7% per cent rate, found
Bochon and Guertzi (1960) near 99.7% per cent rate, found
of the total rate of fracture further chance. The particles were measured.
meant, until took X-ray of titine and X-ray and bottom near the fracture.
worked with certain zone A of the quenching with already
with certain zone A of the quenching with already
Klann and Snow (1977) reported only face-centered cubic, a
and
in 1977 (1963) reported a mixture of the two phases in certain cold-pressed particle before
and hexagonal zirconate will not in mixture of the two forms. Hilt (1967)
reported a mixture of the two phases in certain cold-pressed particle before

I. General introduction

X. Certain
the transition to the condensed face-centered cubic. Lawson and Tang (1949) were not successful in obtaining the low temperature transition in 99.9 per cent pure cerium but were successful at room temperatures by subjecting the metal to a pressure of 15,000 atmospheres. Pauling suggested to Schuh and Sturdivant that the transition might be accounted for by the shift of a 4f electron to a valence state.

2. **Magnetic properties**

La Blanchetais (1945) found, as had other workers, that metallic cerium of face-centered cubic structure showed an anomaly in its magnetic susceptibility at 110° K. Cooling to 80.7° K. and warming resulted in a hysteresis loop in the magnetic susceptibility-temperature curve. Such a transition was not observed for the hexagonal form. The face-centered cubic form followed the Curie law of paramagnetism above 110° K. with a Curie temperature of -51° K. and a Curie constant, C, of 58.68 x 10^-4. This constant is in units such that, for \( x(2-\theta) = C \), \( x \) is the magnetic susceptibility per gram. The cerium metal used by La Blanchetais was 99.6 per cent pure with the principal impurity being silicon. It contained 0.0005 per cent iron.

3. **Resistivity**

James, Legvold and Spedding (1953) have studied the electrical resistivity of cerium metal in the temperature range from 300° K. to 2° K. They found that the electrical resistivity decreased sharply as the temperature was lowered below 110° K. This was attributed to the transition from the normal face-centered cubic structure to the so-called condensed
face-centered cubic structure with reduced lattice parameter. Cooling to helium temperatures and warming resulted in a hysteresis loop in electrical resistivity, with the resistivities obtained while warming being lower than those obtained while cooling. The lower temperature limit of the loop was near 40° K. and the upper limit near 180° K.

4. Specific heat

Parkinson, Simon, and Spedding (1951), in studying the specific heat of cubic cerium, found anomalous behavior in the temperature range from 120° K. to 180° K. It was suggested by them that the anomaly, which included thermal hysteresis of the specific heat, could be associated with an incomplete transition to the condensed cubic state accompanying the transition of a 4f electron to a 5d state.

5. Dilatometry

Dilatometric studies of metallic cerium of 99.6 per cent purity by Trombe and Foex (1945) have shown that face-centered cubic cerium undergoes a sharp decrease in volume at about 120° K., the amount of the decrease being greater than 10 per cent of the volume. The length of a rod, plotted as a function of temperature, shows a hysteresis loop, with lengths measured while warming being lower than those measured while cooling. The upper temperature limit of the hysteresis loop is near 225° K. with the sharpest rate of increase of length while warming being around 175° K. The decrease in volume was correlated by Trombe and Foex with the anomaly in the paramagnetic susceptibility of cerium metal.
6. **Hall effect**

The Hall effect in cerium metal of unstated purity and structure was studied at room temperature by Smith (1916) and a value of the Hall coefficient, $V_H$, was found to be $+1.22 \times 10^{-12}$ volt-cm/amp-cm. The method of measurement was a d.c. method using a galvanometer to measure the Hall voltage.

**F. Praseodymium**

1. **Crystal structure**

The crystal structure of metallic praseodymium has been variously reported. Rossi (1932) reported the finding of the hexagonal structure in 99.4 per cent pure praseodymium. Kleem and Bommer (1937) reported finding face-centered cubic structure in praseodymium metal of unstated purity. Again, Kleem and Bommer (1939) reported the hexagonal structure if extra lines were indexed by doubling the c-axis. The intensities of the lines did not correspond to true hexagonal structure. The praseodymium used by them was 98 per cent pure with lanthanum being the principal impurity. Heating to 300° C. and 400° C. was not successful in converting the metal to one known structure. Ziegler (1949) worked with praseodymium containing 37 per cent lanthanum and reported an unknown structure.

2. **Magnetic properties**

The paramagnetic susceptibility of praseodymium has been studied by Kleem and Bommer (1939) in the temperature range 90° K. to 393° K. The
metal was embedded in a matrix of the rare earth chloride. They obtained a value of 0° K. for the Curie temperature, and a value of $1.07 \times 10^{-2}$ for the Curie constant, expressed in units per gram.

9. Neodymium

1. Crystal structure

Structure studies of metallic neodymium have resulted in much the same uncertainty as in the case of praseodymium. Quill (1932), working with filings, reported the hexagonal structure for neodymium of unstated purity. Kleem and Bommel (1939) reported finding the hexagonal structure but doubling of the c-axis was required for complete line indexing. The metal used by them was free of other rare earths.

2. Magnetic properties

Neodymium has been studied for its magnetic properties by Trombe (1937) from room temperature down to 70° K. The paramagnetic susceptibility was observed to obey a Curie law from room temperature down to 110° K., below which it increased more rapidly with decreasing temperature. In the temperature region below 110° K., the reciprocal susceptibility was not a linear function of temperature but was slightly concave upward. Trombe reported that an extrapolation to lower temperatures indicated a paramagnetic Curie temperature at about 70° K. For the upper temperature region between 110° K. and 300° K. the Curie temperature was found to be 11° K. and the Curie constant was found to be $1.11 \times 10^{-2}$ in units per gram.
H. Gadolinium

1. Crystal structure

Gadolinium has been reported by Klemm and Bonner (1937) to have the hexagonal structure. The metal studied by them was 99.5 per cent pure. Banister, Barson, Legvold and Spedding (1953) report the hexagonal structure for gadolinium to 100° K.

2. Magnetic properties

Metallic gadolinium has been observed by Trombe (1937) to be paramagnetic above 16° C. and to obey a Curie law of paramagnetism above 100° C. The paramagnetic Curie temperature was observed to be 39.5° C. and the Curie constant, in units per gram, was observed to be .050.

I. Dysprosium

1. Crystal structure

Dysprosium has been investigated by Klemm and Bonner (1937) and found to be of hexagonal structure. Banister (1953) has found dysprosium metal to show the hexagonal structure from room temperature to about 46° K.

2. Magnetic properties

Trombe (1945) has reported that the paramagnetic susceptibility shows a remarkable behavior in the temperature region around and below 180° K. Working with dysprosium which was of better than 99 per cent purity, he found a maximum in the paramagnetic susceptibility as a function of
the curie constant in $10^7 \text{C}^2 \text{e}^{-}$ units.

The results were found to be quite dependable. They revealed the curie temperature
in the range of 150° to 230° C. The magnetic susceptibility of a certain substance had
been measured at a number of points on a matrix of the curve

The computed mean (1927) standard the magnetic properties of the material

2. Magnetic Susceptibility

The structure of room temperature and down to 0°.

The results, reported (1927) reported magnetic and electrical properties
by Klemm and Klemm (1926) both reported the

Graphs have only been reported in these magnetic structures.

1. External Magnetic

The curie constant was $10^7 \text{C}^2 \text{e}^{-}$ units per gram.

The per cent magnetic Curie temperature was 150° C, and

the per cent magnetic Curie temperature above 200° C.

The per cent magnetic Curie temperature was found, with reasonable and satisfactory agreement.

The results were found to be quite dependable. Below 150° C, evidence of

per cent magnetic Curie temperature.
III. MATERIALS AND APPARATUS

A. Preparation and Analysis of Samples

The rare earth metals were vacuum cast in tantalum crucibles after reduction by calcium in tantalum crucibles and purification with water (Spedding and Damm, 1952). Rough plates were cut from castings of the metals and these were filed to the final form of the Hall samples which was that of a rectangular parallelepiped approximately 2.4 x 0.5 x 0.1 cm. in dimension.

Some of the metals were given various heat treatments which has been reported to leave the metal in one structure form. Metal samples to be annealed were wrapped in tantalum foil and sealed under high vacuum in a quartz tube containing lanthanum turnings as a getter. After heating the getter, the sealed capsule was placed in an oven where the annealing was done.

The purity of each metal was determined by a spectrographic analysis and the results are shown in Table 1 of the Appendix.

Because of the reported allotropy in lanthanum, cerium, and praseodymium, a companion sample of each of these metals was subjected simultaneously to the thermal treatment given the Hall sample. Needles were filed from these companion samples after each significant thermal treatment, sealed in glass capillaries to prevent oxidation, and subjected to X-ray crystallographic analysis to determine, if possible, the structures at each stage in the history of the samples. The intention was to correlate observed changes of the Hall effect with changes of crystal structure. No
change in the structure of cerium was found to be caused by the filing operation. Needles of cerium which were filed after annealing gave the same X-ray patterns as did needles which were annealed after filing. The results of the X-ray analyses are presented along with the results of the Hall effect measurements for each of the metals analyzed.

A record of the history of each sample as regards its annealing and cycling to low temperatures is presented in Table 2 of the Appendix.

B. Temperature Control

Various temperatures for the samples were obtained by boiling either liquid hydrogen or liquid nitrogen and passing the evaporated gas over the sample. A schematic diagram of the dewar and sample holder, with the evaporation and sample heaters, is shown in Figure 1. By controlling the evaporation rate as well as the rate at which heat was introduced by the sample heater, temperatures between 20.3° K. and 300° K. could be obtained. For the higher temperatures, except in the case of cerium where it was necessary for the temperature to change continuously without reversal, liquid nitrogen was used. The lowest temperatures were obtained by raising the liquid level until the sample was immersed in liquid hydrogen. The temperatures could easily be held constant to 0.1° K. during the time required to take a set of readings. A temperature traverse from 300° K. to 30.3° K. and back could be made with about two liters of liquid hydrogen. A photograph showing the experimental arrangement may be seen in Figure 2. The glass dewar is in position between the magnet pole pieces at the left-center of the picture, and at the left is the liquid hydrogen storage vessel with a transfer tube leading to the dewar.
Figure 1. Schematic diagram of sample holder, dewar, and magnet
The magnetic moment of the electron was measured at the center of the \( R \) and \( R \) points of the experiment. The magnetic moment was found to be consistent with a previous measurement by Stern and Gerlach. The magnetic moment was found to be the same for both positive and negative electrons. The magnetic moment was found to be independent of the applied field. The magnetic moment was found to be the same for both positive and negative electrons.

The magnetic moment was measured at the center of the experiment. The magnetic moment was found to be consistent with a previous measurement by Stern and Gerlach. The magnetic moment was found to be independent of the applied field. The magnetic moment was found to be the same for both positive and negative electrons.
II. Sample Holder

The sample holder is shown in its position inside the glass dewar and between the magnet pole pieces in the schematic diagram, Figure 1. One of the serious difficulties encountered in applying an alternating current method to the study of the Hall effect in metals is that of vibration. Because the Hall effect is small in metals, rather large primary currents must be employed in order to obtain a measurable Hall voltage. As a consequence, high alternating currents must flow in a region of high magnetic field, and large forces are exerted on the sample and connecting wires. These large periodic forces may result in vibration of parts of the circuit and also of the holder as a unit.

The first thing that must be ensured is that the physical locations of primary current elements with respect to the voltage pickup circuit elements do not change. If vibration allowed this to happen, the mutual inductance between current and Hall voltage circuits would be time-dependent when the magnetic field was turned on and a spurious voltage would appear in the Hall voltage circuit. To ensure that the mutual inductance not change, care must be taken that the sample and connecting wires be rigid. This was done by firmly holding the metal samples in a heavy clamp of copper and brass which formed part of the primary current circuit. This clamp was fastened tightly to the supporting piece of plastic material as shown in Figure 4.

The second thing of importance is that the rigid holder system not vibrate as a unit in the magnetic field. If it were to do so, the Hall voltage circuit would have threading it, effectively, an intense , time-
varying magnetic field of the same frequency as the Hall voltage, and
again a spurious voltage would result. At ordinary temperatures this
problem could be solved by wedging the holder to the magnet pole pieces,
but when working at low temperatures the necessity for thermal isolation
precludes this possibility.

To prevent vibration of the holder as a unit the holder was mounted
at the lower end of a synthane plastic tube which, supported at the top,
extended down into a dewar holding the low-boiling liquid (see Figure 1).
Synthane tubing was chosen for the support piece because of its mechanical
rigidity, magnetic properties, and low thermal conductivity. The drawing
in Figure 3 shows how the synthane plastic tube was supported at the top.
The entire assembly provided a rigid support for the sample holder and in
addition served as a gas-tight dewar cap. The complete sample holder unit
could be removed easily by loosening a few screws at the top. Every
effort was made to minimize magnetic moment in the primary current circuit.
Connecting wires were twisted and the current lead to the lower end of the
sample was divided so that two approximately equal and opposite magnetic
moments resulted (Figure 4). This split conductor was cut in one piece
from copper sheet to make sure that the two current paths were as nearly
as possible of the same resistance. With this type holder, Hall voltages
in copper were linear with magnetic field to 15,000 oersted. The effect
of vibration would be to cause a quadratic field dependence, and this was
observed in other types of holders.

The problem of making reliable, low resistance contacts to rare earth
metals is a serious one because of their tendency to oxidize. After
Figure 3. Dewar cap and sample holder support assembly
Figure 4. Sample holder with metal sample in position
attempts to evaporate and weld contacts to the metals, and to solder to
them, were abandoned, the method of making contact by means of tungsten
spring contacts was adopted for the Hall voltage contacts. Three sharp
tungsten wires, pressed under bending against the sides of the metal sample
(see Figure 4), provided contacts of negligible resistance over the widest
temperature ranges studied and for as long periods of time as were found
necessary.

Because the resistivity of rare earth metals is rather high, the
positioning of Hall voltage contacts on either side of the sample to the
condition of equipotentiality is quite difficult. The failure to achieve
this setting can result in large voltages in zero magnetic field which are
many times larger than the Hall voltage and which make measurements impos-
sible. The need to have some means of adjusting the setting becomes
especially important when measurements are carried out over a wide tempera-
ture range and differences in thermal expansion cause shifts of the contacts.

To afford effective adjustment of the Hall voltage contacts, a three-
contact method was adopted. In this method, one contact is placed at one
edge of the sample, two at the opposite edge, and the two are connected to
a potentiometer. The Hall voltage is taken from the single tungsten con-
tact and the movable contact of the potentiometer, and by adjusting the
potentiometer the adjustment to equipotentiality is effected. A schematic
diagram of this system is shown in Figure 5. The system was found to be
quite satisfactory and extremely useful since significantly large changes
in the setting of the potentiometer, which was a helipot, were necessary
in going from 300 K. to 20 K.
E. Electronic Equipment

The electronic apparatus consisted of: a 100 c.p.s. narrow band amplifier, by means of which the Hall voltage was amplified to a measurable level; a 100 c.p.s. oscillator-power amplifier which supplied primary current to the Hall samples; regulated power supplies; and an oscillograph. The output of the amplifier was viewed, and measurements were made on, the screen of the cathode ray oscillograph. A block diagram of the electronic equipment is shown in Figure 5 and the components can be seen mounted on the panel rack at the right in Figure 2.

The narrow band amplifier had a half-power band width of 1 c.p.s. at 100 c.p.s. and a voltage gain of approximately $4 \times 10^3$. The noise level was about $5 \times 10^{-9}$ volts, referred to the input. The narrow band characteristic was attained through use of two parallel-tee networks located in feedback circuits in a high gain amplifier. Good stability was assured through use of negative feedback. A diagram of the amplifier and oscillator-power amplifier circuit is shown in Figure 6. Filaments were heated by a regulated d.c. power supply, one side of the filament of the first amplifier tube being grounded. Care was taken in all cases that no 100 c.p.s. currents flowed in shields and chassis.

The 100 c.p.s. oscillator-power amplifier was capable of delivering up to 5 amperes of current at low distortion to the primary current circuit, the impedance of which was of the order of 0.3 ohm. In all cases, the current used during Hall effect measurements was about 1 ampere. The frequency of the oscillator could be varied slightly about 100 c.p.s. in order to tune to the center frequency of the amplifier response curve. The
Figure 5. Block diagram of electronic equipment
Figure 6. Circuit diagram of amplifier and current supply oscillator-amplifier
IV. RESULTS AND DISCUSSION

The results of the work on each metal are presented separately. The results of spectrographic analysis for the presence of impurities can be found in Table 1 of the Appendix, and a history of each sample can be found in Table 2 of the Appendix, and the symbols on the graphs refer to this table.

In all cases, the Hall effect is represented by the factor \( \frac{V_H t_o}{H_0} \) where \( V_H \) is the Hall voltage measured in volts, \( t_o \) is the room temperature thickness of the sample in cm., \( I \) is the primary current in amperes, and \( H_0 \) is the applied magnetic field in oersteds. Only in the case of cerium might one expect the actual thickness of the sample at any temperature to be significantly different from \( t_o \), but in cerium the transition to the condensed phase can be expected to decrease \( t_o \) by 6 per cent.

The effect of magnetization is included in the term \( \frac{V_H t_o}{H_0} \) and one must interpret the results with this in mind. When reference is made to a Hall coefficient it will be understood to mean \( \frac{V_H t_o}{H_0} \).

For each metal, magnetic effects are taken into account as well as possible and a value obtained for the ordinary Hall coefficient, \( R_o \). From \( R_o \) is calculated the effective number and type of carrier according to one-band free electron theory, and in addition the two-band theory is applied to obtain a relation between the number of holes, \( n_h \), in the s-band and the mobility ratio \( \mu_h/\mu_s \). These relations for all the metals studied
are shown on one graph in Figure 15. In every case it was assumed that conduction is by holes in the 6s band and by electrons in the 5d band.

A. Lanthanum

The Hall effect in lanthanum metal was studied over the temperature range from 20.3° K. to 300° K. At all temperatures the effect was negative and the Hall voltage was found to be linear with field at 20° K., 78° K., and 300° K.

Measurements made on a cast, unannealed sample resulted in a value of

\[ \frac{V_{H,a}}{H_a} = -0.35 \times 10^{-12} \text{ volt-cm/amp-cm} \]

for the Hall coefficient. Annealing at 350° C. raised this value to about \(-0.8 \times 10^{-12}\). The value was sensitive to further heat treatments, but did not depart by more than 10 per cent from this value of \(-0.8 \times 10^{-12}\) at room temperature.

The sample was annealed 97 hours at 370° C. and quenched to room temperature in an attempt to get only the face-centered cubic structure. This heat treatment has been reported by Ziegler (1943) to yield the face-centered cubic structure only. Various X-ray analyses were made of a companion sample which had been subjected to identical and simultaneous heat treatments with the Hall sample, and in no case could a change in line intensities be correlated with a change in the magnitude of the Hall effect. The existing structure could not be clearly determined. The positions of the lines in the diffraction pattern indicated that most corresponded to the hexagonal structure, but the intensities were not correct for a true hexagonal structure. Possible modification of the intensity distribution caused by coincidence of cubic and hexagonal lines seemed to be ruled out
by the fact that a strong, non-coinciding cubic line was completely missing. The structure study can be summed up by the statement that the structure could not be determined and no correlation could be made between changes in the Hall effect and changes in structure.

A typical curve of the Hall effect as a function of temperature is shown in Figure 7. All curves showed about the same temperature dependence but the magnitudes were different depending on the heat treatment. This one is shown as representing the temperature dependence and as being approximately of average magnitude. The magnitude of the Hall effect shows a marked temperature variation, reaching a maximum at about 190° K. and going through a minimum at about 40° K. before rising sharply to a value near the room temperature value at 20.3° K.

The increase in the Hall effect below 40° K. could conceivably be interpreted as the rise occasioned by the approach to a Curie point with the accompanying increasing extraordinary effect. The magnetic properties of metallic lanthanum have been studied only to liquid air temperatures and it has been found to be weakly paramagnetic. The electronic structure of the free atom, with the absence of 4f electrons, would indicate that the paramagnetism is weak at all temperatures. A shift of an electron to a 4f state at low temperatures might be expected to result in stronger paramagnetism, but should at the same time be accompanied by a marked change in the Hall coefficient. On the other hand, all of the temperature variation could be understood on the basis of the two-band theory of the Hall effect, if one assumed that the ratio of the mobilities is temperature dependent.
Figure 7. Hall coefficient of lanthanum as a function of temperature
The curve shows the number of holes in the ge book as a function of the temperature. The condition is that the book needs to be in the correct position for the book to stand. The curve is plotted in Figure 1. This curve is plotted for several different cases:

1. Certain
2. Certain
3. Certain

The effective number of contacts before the separation of the book and the book is determined in both cases. Since the free space contactation above three separations in the book is constant, the curve indicates a value of 0.6 x 10^17 watts/cm^2-cm-sected. The book temperature, a value of 0.6 x 10^17 watts/cm^2-cm-sected.
Figure 8. Hall coefficient of cerium as a function of temperature
be found of the presence of hexagonal structure. This would indicate that the lower room temperature value of the Hall coefficient after cooling is not due to the presence of hexagonal structure. The lower value may be associated with the presence of dislocations introduced by the cooling and consequent transitions to the condensed state. Reannealing always brought the room temperature Hall coefficient back up to the higher value.

The sudden change of the coefficient around 110° K. and 130° K. can be correlated with similar reported changes in resistivity, magnetic susceptibility, and lattice parameter. This change could mean that these anomalies are accompanied by a sudden change in the effective number of carriers. This could be considered direct evidence that there is a transition of an electron from a 4f state to a 5d state as suggested by Pauling. Hole conduction predominates and the transition of an electron to a 5d state might result in a greater electronic contribution, reducing the magnitude of the Hall effect.

The gradual increase as the metal is cooled to 110° K. might at first be thought to be a magnetic effect but the magnitude of the increase is incompatible with the existing magnetic data for cerium.

The lower branch of the curve, before the break at 130° K., appears to be approaching a higher temperature value near $1 \times 10^{-12}$ volt-cm/ampere. The high temperature limit of the upper branch seems to be about the same. If the two branches, upper and lower, represent two states having different effective numbers of carriers, it is difficult to see why the high temperature limits of the Hall coefficients should be the same.
The value of the system constant on the upper branch at 100°C cannot be underestimated.

The slope constant at the upper branch is shown in Figure 2 for this case.

The value of the system constant on the upper branch at 100°C can be calculated as:

\[ I = I_0 + \frac{\Delta I}{\Delta T} T \]

where \( I \) is the upper branch value at 100°C, \( I_0 \) is the value at 10°C, \( \Delta I \) is the change in current, and \( T \) is the temperature in °C.

The upper branch value at 10°C can be calculated as:

\[ I = I_0 + \frac{\Delta I}{\Delta T} T \]

where \( I_0 \) is the lower branch value at 10°C, \( \Delta I \) is the change in current, and \( T \) is the temperature in °C.

The value at the upper branch at 100°C can be calculated as:

\[ I = I_0 + \frac{\Delta I}{\Delta T} T \]

where \( I \) is the upper branch value at 100°C, \( I_0 \) is the value at 10°C, \( \Delta I \) is the change in current, and \( T \) is the temperature in °C.
properties for ceria. It appears to be something independent of the postulated electron transition since the transition causes the Hall coefficient to change in the opposite sense.

C. Praseodymium

The Hall effect in metallic praseodymium was positive at all temperatures between 20° K. and 300° K. and the effect was linear with magnetic field to 6000 oersteds at 300° K., 78° K., and 20° K.

X-ray analyses made before and after various annealing processes revealed no definite structure changes. As in the case of lanthanum, the line positions on the diffraction pattern corresponded to the hexagonal structure but the intensity distribution was not correct for that structure.

The experimental results are shown in Figure 9. The results were reproducible after various heat treatments both as to magnitude and temperature variation. The average room temperature value for $V_{H} = \frac{1}{3}$H$_{0}$ was found to be $+ (0.709 \pm 0.006) \times 10^{-12}$ volt-cm/amp-oersted.

The temperature variation was slight down to about 100° K. and then increased gradually in a manner suggesting that the extraordinary effect was becoming appreciable. Magnetic measurements of Klemm and Besemer (1939) indicate a paramagnetic Curie point at 0° K. so the interpretation can be made that $R_{0}$ remains practically constant throughout this temperature range and that the increase at low temperatures is caused by the magnetic effect.

The room temperature value of $+ 0.709 \times 10^{-12}$ for the Hall coefficient indicates that hole conduction predominates. A one-band interpretation would require 3 holes per atom to explain this result, and it is not
Figure 9. Hall coefficient of praseodymium as a function of temperature.
Figure 10. Hall coefficient of neodymium as a function of temperature.
the possibility of a Curie temperature near 70° K., the temperature at
which the maximum in the Hall coefficient occurs. An alternative explana-
tion would be the temperature dependence of the mobility ratio \( \mu_2/\mu_3 \) in the
two-band theory of the Hall effect.

The positive sign of the Hall coefficient at room temperature indicates
positive hole conduction predominating and the magnitude, on a one-band
theory, corresponds to 2.1 holes per atom contributing to conduction.
Assuming electron conduction in the 5d band and hole conduction in the 6s
band, and assuming no contribution to conduction by 4f electrons, the two-
band theory could be used. If one requires that \( n_d = n_s + 1 \), and applies
the two-band theory, the result is a relation between \( n_s \), the number of
holes in the 6s band, and \( \mu_d/\mu_s \). This result is shown graphically in
Figure 15.

E. Gadolinium

The Hall effect in gadolinium was studied in the temperature region
between 20° C. and 350° C. The results are shown in Figure 11 where
\( V_{H0}/IH_0 \) is plotted as a function of temperature. The sign of the effect
throughout this range is negative.

Trombe (1937) has reported that gadolinium has a paramagnetic Curie
point at 29.5° C. and a ferromagnetic Curie point at 16° C. Above 100° C.,
according to Trombe, the magnetic susceptibility obeys a Curie law. The
increase of \( V_{H0}/IH_0 \) as the Curie temperature is approached may be inter-
preted as being caused by an increasing extraordinary Hall effect accom-
ppanying an increasing magnetization.
Figure 11. Hall coefficient of gadolinium as a function of temperature
If one takes the expression for the Hall effect in a paramagnetic material, sets \( R_0 = -0.4 \times 10^{-12} \), \( \alpha = 550 \), and uses the values for the magnetic susceptibility of Treube, then one can obtain calculated values of \( V_{H0}/H_0 \) as a function of temperature. They agree fairly well with the observed values above 100° C, but tend to fall below the experimental curve for lower temperatures. This may indicate that \( \alpha \) is not a constant but increases slightly as the Curie temperature is approached. In the case of nickel it was found that \( R_0 \) remains constant through the Curie temperature (Bostoker and Pugh, 1951). The assumed constancy of \( \alpha \) is different from the conclusions of Pugh, Bostoker and Schindler (1950) who analyzed the data of Smith and, on the basis of magnetic saturation determination of \( \alpha \), considered that it decreased rapidly to zero above the Curie temperature for nickel. However, in a true paramagnetic region, one would not be able to detect the extraordinary effect by a magnetic saturation method using moderate fields, even though it was present.

The method used here for determining \( R_0 \) is not a very precise one since the extraordinary effect dominates the ordinary Hall effect in this temperature range. The good agreement of the calculated values with experimental values over such a wide temperature range would seem to indicate that the results are correct order of magnitude.

If one takes \( R_0 = -0.4 \times 10^{-12} \) volt-cm/amp-oersted, then a one-band free electron theory leads to a value of 4.8 electrons per atom contributing to conduction. The two-band theory, along with the condition that \( n_g = n_b + 1 \), leads to a relation between \( n_g \) and \( \mu_A/\mu_B \), which is shown in Figure 15.
the other

The effect of the parameter c, 
magnetic a change from one magnetic shape to
superconducting decrease and reacted of the effect may be due to a change in
which the magnetic in the parameter a phase transition of the parameter c
effective with each stage of magnetic, the effect on the shape the c to the experience of the magnetic energy in dependence and one which shape the
case of magnetic superconducting evolution temperature. This may be due
effect of magnetization. Assume (I1966) becomes a maximum at 120°K. in
where due to the effect on a cation point which the magnetic Energiestage
The interaction between 300° K. and 20° K. appears to be

The field causing a resistance drop as in Figure 12.

We find that our theory and experiment, the Hall voltage in a function
consistent agreement below their experimental, the Hall voltage at 120°K. and above 300°K. the effect of
Hall coefficient was fixed depends on below 120°K. and dependence of
appears in Figure 12. The effect was not seen in the temperature range

A plot of the Hall coefficient, $\frac{dH_\parallel}{dI}$, as a function of temperature

$\Delta$.
Figure 12. Hall coefficient of dysprosium as a function of temperature
Figure 13. Hall voltage as a function of applied field in dysprosium at 127° K.
applied, along with the condition that $n_d = n_s + 1$, the relationship between the number of holes in the 6s band, and the mobility ratio, $\mu_d/\mu_s$, is obtained and this is shown in Figure 15.

6. Erbium

The Hall coefficient of metallic erbium was measured in the temperature range from 100° K. to 300° K. A graph of the Hall coefficient as a function of temperature is shown in Figure 14. The effect was negative at all temperatures and increased in magnitude as the temperature was lowered. This increase could be associated with the effect of magnetization as the Curie temperature, reported by Kleen and Bommer (1937) to be at 40° K., is approached.

The value of the Hall coefficient at room temperature was found to be $-0.341 \times 10^{-12}$ volt-cm/amp-cerated but the indication is that there may be some magnetic effect even at room temperature. The assumption of constant $n_s$ and the use of published magnetic properties in the expression for the Hall effect in a paramagnetic material are not successful in obtaining a calculated curve which fits closely the experimental curve.

If one takes the room temperature value of the coefficient to be the ordinary Hall coefficient, $R_0$, then this corresponds to 2.1 electrons per atom contributing to conduction if one band is involved. Applying the two-band theory and the condition that $n_d = n_s + 1$, one obtains the curve for $n_s$ as a function of the mobility ratio $\mu_d/\mu_s$, which is shown in Figure 15.
Figure 1.4. Hall coefficient of erbium as a function of temperature.
Figure 15. Number of holes in the $da$ band as a function of the mobility ratio from the two-band theory of the Hall effect.
E. General Remarks

There is no apparent regularity in the change in the ordinary Hall coefficient along the rare earth series as was observed in the case of the transition elements of the fifth and sixth periods.

It is possible to account for the observed values of the Hall coefficients by assuming electron conduction in the 5d band and hole conduction in the 6s band. This assumption, with the condition that there are three electrons per atom available for both bands (except in the case of condensed cerium where it is assumed that there are four electrons available), and the two-band theory of the Hall effect, leads to a relation between the number of holes in the 6s band and the ratio of the d-band mobility to the s-band mobility, $\mu_d/\mu_s$. This relation is shown plotted in Figure 15 for each of the metals studied.

It can be seen that $n_s$, the number of holes per atom in the 6s band, is double-valued for some $\mu_d/\mu_s$ in the case of the metals having positive Hall coefficients. Also, if one assumes one value of $\mu_d/\mu_s = 0.1$, it is possible to account for all the observed Hall coefficients by choosing appropriate values for $n_s$. For all but cerium, $n_s$ would be very nearly zero, corresponding to a nearly-full 6s band.

Alternatively, one could account for the observed Hall coefficients by assuming one value for $n_s$ and choosing appropriate values of $\mu_d/\mu_s$ in each case. For those metals having negative Hall coefficients, no upper limit is imposed on $\mu_d/\mu_s$ except that there must be hole conduction in the 6s band.
V. SUMMARY

Measurements of the Hall effect in metallic lanthanum, cerium, praseodymium, and neodymium were carried out in the temperature range from 20.3° K. to 300° K. For gadolinium, dysprosium, and erbium, the measurements were made quantitatively only above the respective Curie temperatures, the range of temperatures for gadolinium being from 30° C. to 350° C. Insofar as possible, magnetic effects were taken account of and values obtained for the ordinary Hall coefficients. The results for each metal are summarized below.

1. Lanthanum showed an unknown crystal structure and the magnitude of the Hall coefficient was strongly dependent on heat treatment. As received, the Hall coefficient at room temperature was \(-0.35 \times 10^{-12}\) volt-cm/amp-cersted, after annealing it was about \(-0.3 \times 10^{-12}\) volt-cm/amp-cersted, and was changed by further annealing. The Hall effect showed some rather large variations in magnitude with temperature but remained negative in sign at all temperatures studied.

2. Cerium exhibited nothing but face-centered cubic structure at room temperature after either annealing or cycling to low temperatures. The room temperature value of the Hall coefficient after annealing was \(+1.31 \times 10^{-12}\) volt-cm/amp-cersted and this was reproducible for various samples to better than 1 per cent. The value at room temperature after the first and subsequent cycles to low temperatures was \(+1.41 \times 10^{-12}\) volt-cm/amp-cersted. Reannealing raised this back up to the higher value.
The Hall coefficient, which was positive at all temperatures, showed a thermal hysteresis with sharp changes in magnitude near 100° K. on cooling and near 180° K. on warming. These sudden changes could be considered evidence for the postulated shift of a 4f electron to a 5d state.

3. Praseodymium was of undetermined structure. The room temperature Hall coefficient was \( +0.709 \times 10^{-12} \) volt-cm/amp-oersted and was not sensitive to annealing and cooling. There was little temperature variation of the coefficient except below nitrogen temperatures and this may have been due to a magnetic effect.

4. Neodymium was found to have a room temperature Hall coefficient of \( +0.871 \times 10^{-12} \) volt-cm/amp-oersted which was not affected by annealing and cooling. A rather complicated temperature dependence was found at the lower temperatures with a small maximum at near 70° K. and a sudden rise near 30° K. Both may be due to magnetic effects.

5. The Hall effect in gadolinium was negative in the range of temperatures between 30° C. and 350° C. After taking account of the extraordinary effect, a value was obtained for \( R_0 \), the ordinary coefficient, of \( -0.4 \times 10^{-12} \) volt-cm/amp-oersted.

6. Dysprosium showed a negative Hall effect at room temperature and this increased in magnitude down to about 200° K. below which temperature it decreased and reversed sign. This reversal was attributed to the extraordinary effect. An approximate value for the ordinary coefficient, \( R_0 \), was found to be \( -1.0 \times 10^{-12} \) volt-cm/amp-oersted.

7. Erbium was found to have a negative Hall effect from room temperature down to 20.3° K. The magnitude of the coefficient at room temperature was \( -0.341 \) volt-cm/amp-oersted.
VI. LITERATURE CITED


VII. ACKNOWLEDGMENTS

The author wishes to express his thanks to Dr. S. Legvold and Dr. F. H. Spedding for their interest in the continuation of this investigation, to Dr. G. C. Danielson and Dr. J. M. Keller for helpful discussions, to Dr. J. Powell and his group for preparing the pure rare earth salts, to Mr. D. Dennison and Mr. E. Barton for the preparation of the metals, to Mr. J. R. Banister and Mr. C. Anderson for their work on the X-ray structure analysis, and to Mr. R. Anderson, Mr. W. Sylvester, Mr. A. Read, and Mr. E. Harris for their help in designing and building equipment.
VIII. APPENDIX
Table 1
Spectrographic Analysis of Metal Samples
Used in Hall Effect Measurements

<table>
<thead>
<tr>
<th>Metal</th>
<th>Analysis*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>Si, 0.1%; Ta, &lt; 0.3%; Ca, 0.05%;</td>
</tr>
<tr>
<td></td>
<td>Fe, 0.02%; other rare earths, not detected</td>
</tr>
<tr>
<td>Cerium</td>
<td>Si, 0.02%; Ca, 0.04%; Nd, 0.03%;</td>
</tr>
<tr>
<td></td>
<td>La, 0.03%; Pr, Ta, not detected</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>Ca, &lt; 0.04%; Nd, 0.06%; other rare earths, not detected</td>
</tr>
<tr>
<td>Neodymium</td>
<td>Ca, &lt; 0.02%; Fe, other rare earths, not detected</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>Ca, &lt; 0.02%; Sm, &lt; 0.06%; Fe, Co, not detected</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>Ca, very weak; Ho, 0.05%;</td>
</tr>
<tr>
<td></td>
<td>Y, 0.02%; Fe, Ta, not detected</td>
</tr>
<tr>
<td>Erbium</td>
<td>Si, trace; Ho, &lt; 0.02%; Y, &lt; 0.02%;</td>
</tr>
<tr>
<td></td>
<td>Ca, Fe, very weak; Ta, not detected</td>
</tr>
</tbody>
</table>

*The sign < indicates that the element referred to was not detected and that the concentration was less than that indicated.
<table>
<thead>
<tr>
<th>Sample</th>
<th>History</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-1</td>
<td>Cast, annealed 97 hours at 370°C, quenched to room temperature</td>
</tr>
<tr>
<td>Ce-1</td>
<td>Cast, annealed 97 hours at 370°C, quenched to room temperature</td>
</tr>
<tr>
<td>Pr-1</td>
<td>Cast, annealed 79 hours at 410°C, quenched to room temperature</td>
</tr>
<tr>
<td>Pr-2</td>
<td>Pr-1, plus: cooled to 20.3 K, annealed 79 hours at 410°C and quenched to room temperature</td>
</tr>
<tr>
<td>Pr-3</td>
<td>Pr-2, plus: cooled to 20.3 K, annealed 79 hours at 410°C and quenched to room temperature</td>
</tr>
<tr>
<td>Nd-1</td>
<td>Cast, annealed 37 hours at 400°C, slow-cooled to room temperature</td>
</tr>
<tr>
<td>Gd-1</td>
<td>Cast, unannealed</td>
</tr>
<tr>
<td>Dy-1</td>
<td>Cast, unannealed</td>
</tr>
<tr>
<td>Er-1</td>
<td>Cast, annealed 45 hours at 500°C, slow-cooled to room temperature</td>
</tr>
</tbody>
</table>