

The Hall Effect in Yttrium, Lanthanum, Cerium, Praseodymium, Neodymium, Gadolinium, Dysprosium, and Erbium*

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The Hall effect has been studied from 300°K to 20.3°K in metallic yttrium, lanthanum, cerium, praseodymium, and neodymium. The ferromagnetic rare earth metals, gadolinium, dysprosium, and erbium have been studied quantitatively only above their respective Curie temperatures with gadolinium being measured to 350°C. The measurements have been made at many temperatures using an alternating current method. Yttrium, lanthanum, gadolinium, and erbium are found to have negative Hall effects at all temperatures studied. Cerium, praseodymium, and neodymium show positive Hall effects throughout the temperature range investigated. Dysprosium metal exhibits a negative Hall effect from 300°K down to about 130°K, but below that temperature the effect is positive. This reversal is interpreted as being due to a change in the sign of the extraordinary Hall effect.

The Hall coefficient of cerium is found to go through a thermal hysteresis loop in a manner similar to the electrical resistivity and other properties. Values for the ordinary Hall coefficients are obtained where necessary from the temperature variation of the Hall effect. The Hall coefficients are used to calculate for each metal the effective number of carriers, n^* , ($n^* = 1/NeR_0$), on a simple one-band model. In addition, the two-band model, assuming electron conduction in the $5d$ band and hole conduction in the $6s$ band, is used to understand the positive effect in three of the metals and to obtain curves for the number of holes in the $6s$ band as a function of the ratio of d -electron mobility to s -hole mobility. No ordered change in the magnitude and sign of the effect along the rare earth series is observed.

I. INTRODUCTION

THE development of methods for preparing highly pure rare earth salts¹ and metals² has made possible the study of the properties of many of the rare earth metals of high purity.

The study of the Hall effect in rare earth elements is of interest because of their electronic structures, which differ principally in the occupation of $4f$ states and not in the occupation of valence states which are ordinarily considered to be the ones which become of importance in electrical conduction. It has been found³ that there is a regular change in the magnitude and sign of the Hall coefficients of the transition metals of the fifth and sixth periods as electrons fill $5d$ and $6d$ states. This investigation was initiated to determine what effect the filling of $4f$ states has on the Hall effect in the rare earth elements. Because of its similarity in electronic structure to the rare earths, the Hall effect in metallic yttrium was also studied.

The temperature range below room temperature was of special interest because many of the metals show abnormal properties in this range. For cerium, in particular, the electrical resistivity,⁴ magnetic suscepti-

bility,⁵ crystal structure,⁶ and thermal expansion⁷ show remarkable behavior in this temperature range. It has been suggested⁶ that this behavior is associated with a shift of an electron between $4f$ and $5d$ states. Since the Hall effect gives information about the numbers and types of carriers of electrical current, it was thought that this study might give evidence supporting or contradicting the hypothesis of a $4f \leftrightarrow 5d$ shift.

Some of the rare earth metals have been reported to show more than one crystal structure. Lanthanum,^{8,9} cerium,^{6,9,10} and praseodymium^{9,11,12} have been reported to exist with both the face-centered cubic (f.c.c.) and hexagonal close-packed (h.c.p.) structures or in mixtures of the two. Because crystal structure may be important to the Hall effect, an attempt was made to determine the crystal structures of the Hall sample metals and to correlate changes in the Hall effect with changes in structure.

Besides allotropy, another property of these metals which affects interpretation of the results of Hall effect measurements is the magnetic property. Several of the metals are ferromagnetic^{9,13,14} and most are rather highly paramagnetic^{5,12,13} in this temperature range. Because magnetization has a strong influence on the Hall effect,¹⁵ one might expect the interpretation of

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¹ F. H. Spedding *et al.*, I. J. Am. Chem. Soc. **69**, 2777 (1947); II. J. Am. Chem. Soc. **69**, 2786 (1947); III. J. Am. Chem. Soc. **69**, 2812 (1947).

² F. H. Spedding and A. H. Daane, J. Am. Chem. Soc. **74**, 2783 (1952).

³ E. Justi and M. Kohler, Abhandl. braunschweig. wiss. Ges. **3**, 44 (1951).

⁴ James, Legvold, and Spedding, Phys. Rev. **88**, 1092 (1952).

⁵ C. La Blanchetais, Compt. rend. **220**, 392 (1945).

⁶ A. F. Schuch and J. H. Sturdivant, J. Chem. Phys. **18**, 145 (1950).

⁷ F. Trombe and M. Foex, Compt. rend. **217**, 501 (1943).

⁸ E. Zintl and S. Neumayr, Z. Electrochem. **39**, 84 (1933).

⁹ W. Klemm and H. Bommer, Z. anorg. u. allgem. Chem. **231**, 138 (1937).

¹⁰ A. W. Hull, Phys. Rev. **18**, 88 (1921).

¹¹ A. Rossi, Nature **133**, 174 (1932).

¹² W. Klemm and H. Bommer, Z. anorg. u. allgem. Chem. **241**, 264 (1939).

¹³ F. Trombe, Ann. phys. **7**, 385 (1937).

¹⁴ F. Trombe, Compt. rend. **221**, 19 (1945).

¹⁵ Pugh, Rostoker, and Schindler, Phys. Rev. **80**, 688 (1950).

TABLE I. Spectrographic analyses of metal samples used in Hall effect measurements.

Metal	Analysis
Yttrium	Al, very weak; Ca, weak; Fe, very weak; Dy, 0.5%; Ho, 0.01%; Tb, 0.29%; other rare earths, not detected.
Lanthanum	Si, 0.1%; Ca, 0.05%; Fe, 0.02%; Ta, other rare earths, not detected.
Cerium	Si, 0.02%; Ca, 0.04%; Nd, 0.03%; La, 0.03%; Pr, Ta, not detected.
Praseodymium	Ca, 0.04%; Nd, 0.06%; other rare earths, not detected.
Neodymium	Ca, 0.02%; Fe, other rare earths, not detected.
Gadolinium	Ca, 0.02%; Sm, 0.06%; Fe, Co, not detected.
Dysprosium	Ca, very weak; Ho, 0.05%; Y, 0.02%; Fe, Ta, not detected.
Erbium	Si, trace; Ho, 0.02%; Y, 0.02%; Ca, Fe, very weak; Ta, not detected.

results to be complicated by the extraordinary Hall effect.

Hall effect measurements were made on metallic, polycrystalline yttrium, lanthanum, cerium, praseodymium, and neodymium in the temperature range from 20.3°K to 300°K. The ferromagnetic metals were studied quantitatively only above their respective Curie temperatures where they are paramagnetic.

Sample purities were determined spectrographically and the results are shown in Table I. In Table II are shown the histories of the samples used and the symbols on the graphs reporting results refer to this table.

II. APPARATUS AND MATERIALS

Measurements of the Hall effect were made using an ac method in which the sample is placed in a steady magnetic field and an alternating primary current flows through the sample at right angles to the field.¹⁶⁻¹⁸

TABLE II. Histories of metal samples used in Hall effect measurements.

Sample	History
Y-0	Cast, unannealed.
Y-1	Cast, annealed 36 hours at 500°C, slow-cooled to room temperature.
La-5	Cast, annealed 97 hours at 370°C, quenched to room temperature.
Ce-1	Cast, annealed 97 hours at 370°C, quenched to room temperature.
Pr-1	Cast, annealed 79 hours at 410°C, quenched to room temperature.
Pr-3	Pr-1, plus: cooled to 20.3°K, annealed 79 hours at 410°C, and quenched to room temperature.
Pr-5	Pr-3, plus: cooled to 20.3°K, annealed 79 hours at 410°C, and quenched to room temperature.
Nd-1	Cast, annealed 37 hours at 400°C, slow-cooled to room temperature.
Gd-0	Cast, unannealed.
Dy-0	Cast, unannealed.
Er-1	Cast, annealed 45 hours at 500°C, slow-cooled to room temperature.

¹⁶ W. F. Leverton and A. J. Dekker, Phys. Rev. 80, 732 (1950).

¹⁷ A. W. Smith, Phys. Rev. 35, 81 (1912).

¹⁸ L. A. Wood, Phys. Rev. 41, 231 (1932).

The resulting Hall voltage is alternating with the frequency of the primary current and can be amplified electronically and measured. In this method, if the frequency is high enough,¹⁷ no correction is required for other thermoelectric, thermomagnetic, and galvanomagnetic effects.

A block diagram of the electronic equipment is shown in Fig. 1. The amplifier gain was approximately 4×10^8 with a noise level, referred to the input, of about 5×10^{-9} volt. The band width was 1 cycle per second, this narrow band characteristic being attained through the use of two parallel-tee feedback networks in the amplifier.

The current supply was capable of delivering up to 5 amperes of current to the sample, and in most cases the measurements were made using primary currents of approximately 1 ampere. The magnet provided fields up to 5600 oersteds and the fields were uniform to better than 1 percent over the region occupied by the Hall samples.

Because of the wide temperature range over which

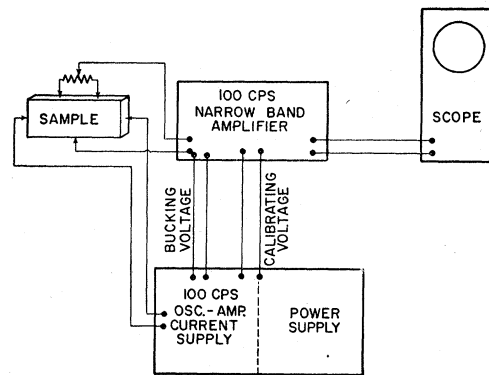


FIG. 1. Block diagram of Hall effect equipment.

measurements were made, it was necessary to provide some means for adjusting the positions of the Hall contacts to equipotentiality. This was done by means of a three-contact method¹⁹ in which this adjustment is made through the use of a potentiometer connected to the double contact (see Fig. 1). By adjusting the movable contact of the potentiometer, one obtains the condition of equipotentiality. Because of the high resistivity of the rare earth metals, this adjustment was very useful since large voltages resulted from slight shifts of the contacts due to temperature changes. After the potentiometer was set for minimum output voltage, with zero magnetic field, the remaining signal was bucked out by means of a small voltage of variable phase and amplitude from a transformer in the current supply circuit.

The impedance of the amplifier input circuit was high compared to the resistance of the Hall samples. For each Hall coefficient determination, the gain of the

¹⁹ F. Kolacek, Ann. Physik 39, 1491 (1912).

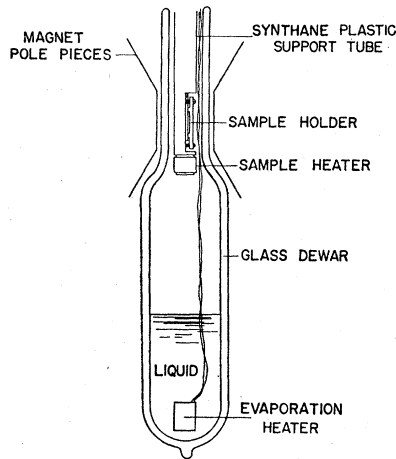


FIG. 2. Schematic diagram of sample holder, Dewar, and magnet.

amplifier was effectively measured by comparing the amplifier output when first the Hall voltage and then the voltage from a standard resistance and voltage divider in the primary current circuit was applied to the amplifier input. The results obtained with this equipment were in agreement with those obtained using a dc potentiometer method and the same sample of gadolinium.

Various temperatures for the sample were obtained by boiling either liquid hydrogen or liquid hydrogen and passing the evaporated gas over the sample (see Fig. 2). By controlling the rate of ebullition and by introducing varying amounts of heat through a heater attached to the sample holder, temperatures between 20.3°K and 300°K could be attained. For the higher temperatures liquid nitrogen was used except in the case of cerium where it was necessary to cause the temperature to change continuously without reversal. The lowest temperatures were obtained by raising the level of liquid hydrogen in the Dewar until the sample was immersed. Temperatures were measured by means of copper-constantan thermocouples fastened to each end of the sample holder. The average of these two was taken to be the temperature of the sample; the greatest temperature difference between the ends of the sample was found to be 4°K. The thermocouples were calibrated at 10°K intervals against a platinum resistance thermometer.

Cancellation of magnetic moment in the primary current circuit and rigid construction of the sample holder and support were used to prevent vibration which would, if it occurred, cause spurious voltages to appear in the Hall voltage circuit. The sample holder was made of copper and brass for rigidity and this was fastened to a supporting piece of Synthane micarta which was, in turn, rigidly supported at the top of the Dewar. The Synthane was chosen for its mechanical strength, low thermal conductivity, and small magnetic susceptibility. Using this type holder and support, the Hall voltage in copper was linear with field up to

15 000 oersteds, the highest field used to test for vibration.

The Hall voltage contacts were tungsten wires with knife edges pressed under bending against the sides of the sample. These contacts provided reliable, low-resistance connections to the sample over long periods of time and throughout the temperature range over which measurements were made. Samples were easily removable for annealing.

Hall samples were cut from the castings and filed to the final dimensions of 2.4×0.5×0.1 cm. Samples to be annealed were wrapped in tantalum foil and sealed under high vacuum in quartz tubes, with lanthanum turnings as a getter. Companion samples accompanied the Hall sample through all heat treatments and needles were filed from the companion samples for x-ray structure analysis.

III. RESULTS AND DISCUSSION

When magnetization is present in a metal sample of the usual form, the Hall coefficient V_{Ht}/IH_0 can be expressed¹⁵ by

$$V_{Ht}/IH_0 = R_0(H + 4\pi\alpha M); \quad (1)$$

where V_H = Hall voltage, t = sample thickness, I = primary current, H_0 = applied field, H = magnetizing field, M = intensity of magnetization, R_0 = ordinary Hall coefficient, and α is a parameter which can be interpreted as a measure of the average magnetic field due to magnetization which acts on conduction particles.

In the neighborhood of the Curie point, values of α for nickel have been found to be of the order of 60; above and below the Curie temperature, α was found to be smaller.¹⁵

In the case of a paramagnetic material, $M = \chi H$, where χ is the magnetic susceptibility, and, for the usual Hall sample, which is a thin plate, $H = H_0 - 4\pi M$. For this case Eq. (1) becomes²⁰

$$V_{Ht}/IH_0 = R_0(1 + 4\pi\alpha\chi)/(1 + 4\pi\chi). \quad (2)$$

When a Curie-Weiss law of paramagnetism is obeyed, the result is

$$V_{Ht}/IH_0 = R_0(T - \theta + 4\pi\alpha C)/(T - \theta + 4\pi C), \quad (3)$$

where θ = Curie temperature, C = Curie constant, and T = temperature.

In a paramagnetic, if α and C are sufficiently large, the measured Hall coefficient at some temperature, i.e., V_{Ht}/IH_0 , would be appreciably different from the ordinary Hall coefficient R_0 , while the Hall voltage would still be proportional to the applied field. In the work reported here, high applied fields were not available so that a test for the condition of linearity with applied field could not be made for fields greater than 5600 oersteds. At all the temperatures at which data

²⁰ N. Rostoker and E. M. Pugh, Phys. Rev. **82**, 125 (1951).

were taken, the Hall voltage was proportional to the applied field.

The experimental curves for the ferromagnetics above the Curie temperatures showed the same general temperature dependence described by Eq. (3) so that, for these rare earth metals, α and C must be large enough to give an appreciable extraordinary Hall effect at temperatures where they are paramagnetic. In a truly paramagnetic region, the ordinary and extraordinary effects would be inseparable by the magnetic saturation method.¹⁵ In this work it was assumed that the metals were paramagnetic and Eq. (3) was used to attempt to separate the two effects by choosing R_0 and α to best fit the experimental curve.

Hall effect data may be interpreted on the basis of a simple one-band theory in which the effective number of carriers per atom contributing to conduction n^* is

$$n^* = 1/NeR_0, \quad (4)$$

where N is the number of atoms per unit volume, e the charge on the carrier, and R_0 the ordinary Hall coefficient. For each metal n^* is calculated from the observed Hall coefficient.

A two-band theory of Mott²¹ developed by Sondheimer²² has been used to understand the observed Hall effect and magnetic properties in nickel¹⁵ and the observed Hall effect in the transition elements of the fifth and sixth periods.³ According to the theory, conduction takes place in two overlapping bands, one nearly full and the other nearly empty. The expression for the Hall coefficient according to this theory can be written

$$R_0 = \frac{1}{Ne} \left[\frac{n_s - n_d \mu_d^2 / \mu_s^2}{(n_s + n_d \mu_d / \mu_s)^2} \right], \quad (5)$$

where N is the number of atoms per unit volume, e the magnitude of the electronic charge, n_s the number of holes per atom in the nearly-full band, n_d the number of electrons per atom in the nearly-empty band, μ_d the mobility of the electrons, and μ_s the mobility of holes.

This relation, with the observed Hall coefficient R_0 and a relation between n_s and n_d , gives n_s as a function of the mobility ratio μ_d/μ_s .

Three of the metals studied were found to have positive Hall coefficients. From the electronic configuration of these elements, it appears that the two-band theory is necessary to explain the result. For each metal, including those having negative Hall coefficients, it was assumed that conduction is by electrons in the $5d$ band, by holes in the $6s$ band, and that there are three electrons available to be distributed between these bands. The $4f$ band is assumed to contribute nothing to conduction. It is to be noted that in the case of the so-called condensed cerium the assumption is made

that there are four electrons available for conduction; this is believed to occur because the $4f$ electron has moved to the $5d$ and $6s$ conduction bands. The consequent relations between n_s and n_d are $n_d = 1 + n_s$ and for condensed cerium $n_d = 2 + n_s$.

In Fig. 3 are shown graphs of n_s as a function of μ_d/μ_s obtained from the two-band expression for the Hall coefficient, the observed ordinary Hall coefficients, and the above assumed relation between n_s and n_d . For those metals having positive coefficients, n_s has two possible values for some choices of the mobility ratio, and there is a maximum value for the mobility ratio, while in the light of the assumptions listed above for those having negative coefficients, the mobility ratio is limited only by the requirement that the $6s$ band be filled to such a level that conduction in this band is by holes.

It can be seen from Fig. 3 that if one were to assume a fixed mobility ratio for all the metals, a value of 0.1 or less would be satisfactory for all observed Hall coefficients, and then differences in magnitude and sign could be attributed to slight changes in n_s in going from element to element. In every case the $6s$ band would be nearly full. A less likely explanation is that n_s is fixed and a different mobility ratio exists for each metal. In all probability only slight variations in μ_d/μ_s occur for the different metals.

A. Yttrium

The Hall coefficient $V_H t_0 / IH_0$, where V_H = Hall voltage, t_0 = room temperature thickness, I = primary current, and H_0 = applied magnetic field, is shown plotted as a function of temperature in Fig. 4. The effect was negative at all temperatures studied, and the Hall voltage was proportional to applied field up to 5600 oersteds at 20.3°K, 78°K, and 300°K. The effect

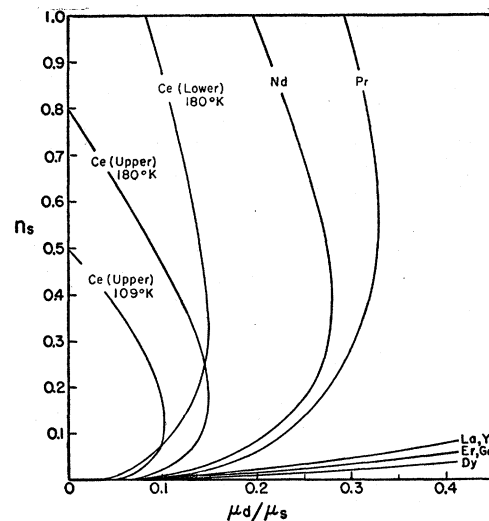


FIG. 3. Number of holes in the $6s$ band as a function of the mobility ratio from the two-band theory of the Hall effect.

²¹ N. F. Mott, Proc. Phys. Soc. (London) **47**, 571 (1953).

²² E. H. Sondheimer, Proc. Roy. Soc. (London) **A193**, 484 (1948).

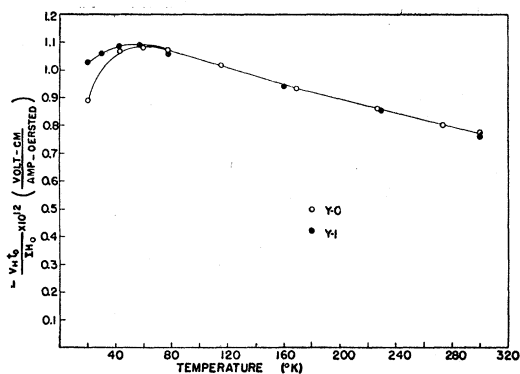


Fig. 4. Hall coefficient of yttrium as a function of temperature.

of annealing (Table II) was to raise the values of the Hall coefficient below 50°K while leaving those above that temperature unchanged.

The room temperature value of the Hall coefficient, -0.770×10^{-12} volt-cm/amp-oersted, corresponds to 2.7 negative carriers per atom effectively contributing to conduction if one assumes the unlikely one-band treatment and uses Eq. (4).

It should be noted that the two-band treatment is capable of accounting qualitatively for the temperature dependence of the Hall coefficient in yttrium since, as the lattice contracts, either the ratio of the number of holes to electrons or the mobility ratio or both, could change.

B. Lanthanum

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

Measurements made on a cast, unannealed sample resulted in a value of -0.35×10^{-12} volt-cm/amp-oersted for the room temperature Hall coefficient. Annealing at 350°C raised this value to -0.8×10^{-12} volt-cm/amp-oersted, and although further heat treatment resulted in additional changes, the magnitude

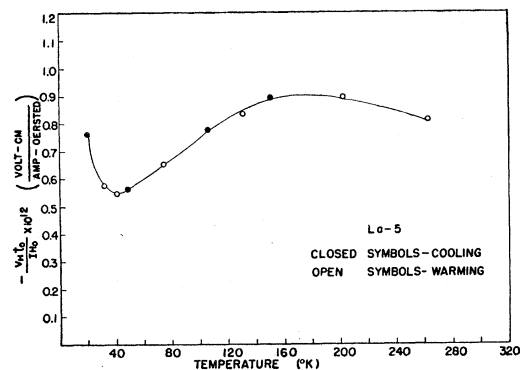


Fig. 5. Hall coefficient of lanthanum as a function of temperature.

did not depart by more than 10 percent from this value of -0.8×10^{-12} at room temperature.

In an attempt to get the metal into the face-centered cubic (f.c.c.) structure, it was annealed 97 hours at 370°C and quenched to room temperature. The x-ray diffraction pattern from a filed needle showed h.c.p. lines but the line intensities were not correct for that structure. Coincidence of f.c.c. and h.c.p. lines could not explain the intensity distribution since a non-coinciding cubic line was missing. No correlation could be made between structure changes and Hall coefficient changes resulting from heat treatments.

A typical curve of the observed Hall coefficient as a function of temperature for an annealed sample is shown in Fig. 5. All curves obtained showed the same temperature variation but the magnitudes were different depending on the heat treatments. The curve shown represents the temperature dependence and average magnitude. The sign is negative as in the case of yttrium, and the effective number of carriers contributing to conduction is very nearly the same in the two cases. The temperature variation is more complex in the case of lanthanum, however, showing both a maximum at 170°K and a minimum at 40°K while yttrium shows only a maximum at about 50°K.

The value -0.8×10^{-12} volt-cm/amp-oersted for the Hall coefficient at room temperature corresponds to a contribution to conduction of 2.9 electrons per atom on a simple one-band model.

C. Cerium

After annealing 97 hours at 370°C and quenching to room temperature, cerium showed only f.c.c. lines and the room temperature Hall coefficient V_{H0}/IH_0 was found to be $+1.81 \times 10^{-12}$ volt-cm/amp-oersted. This was reproducible for several samples within limits of probable error of about 0.5 percent. This result compares favorably with the value $+1.92 \times 10^{-12}$ volt-cm/amp-oersted found by Smith²³ using a dc method.

The room temperature value after the first and subsequent cycles to 20.3°K was about $+1.4 \times 10^{-12}$ volt-cm/amp-oersted. X-ray analysis of the companion sample after cycling to low temperatures showed no evidence of the presence of h.c.p. structure. The low room temperature value after cooling may be due to dislocations produced during the transition to and from the condensed state.⁶ Reannealing and quenching always raised the room temperature coefficient back to the higher value. The Hall effect was positive at all temperatures at which it was observed and the Hall voltage was found to be linear with magnetic field to 5600 oersteds at 20.3°K, 78°K, 100°K, and 300°K.

A graph of the Hall coefficient as a function of temperature, which is typical of several such curves obtained, is shown in Fig. 6. In every case the first cooling after annealing resulted in a curve which was

²³ A. W. Smith, Phys. Rev. 8, 79 (1916).

above those observed subsequently without reannealing. The first cooling curve showed the rapid decrease at a slightly lower temperature than did subsequently obtained curves. The details of the first cooling curve were not as reproducible from sample to sample as were those of the second cooling curve.

The large increase in the Hall coefficient as the metal is cooled to 110°K could be the result of the extraordinary effect, but this seems unlikely. The magnetic susceptibility of cerium is reported⁵ to obey a Curie law in this temperature range with a Curie temperature of -51°K. To show such a large extraordinary effect so far from the Curie temperature would require α to be of the order of 1000 at 110°K if one assumes $R_0 = +1.0 \times 10^{-12}$ volt-cm/amp-oersted. Values of α up to 60 have been reported for nickel¹⁵ in the neighborhood of its Curie temperature.

The sudden decrease of the coefficient near 110°K on cooling and the increase near 180°K on warming can be correlated with reported anomalies in resistivity,⁴ magnetic susceptibility,¹⁵ specific heat,²⁴ crystal structure,⁶ and thermal expansion.⁷ It has been suggested by Pauling⁶ that these anomalies are accompanied by a shift of an electron between 4*f* and 5*d* states.

These changes in the Hall coefficient V_{Ht_0}/IH_0 could be interpreted in at least three ways. First, they could represent changes in the effective number of carriers accompanying the 4*f*→5*d* shift. Second, if the rise of the upper part of the curve is due to the extraordinary Hall effect, then the sudden decrease at 110°K could be due to the decrease or vanishing of magnetic moment in the metal due to the 4*f*→5*d* transition and a simultaneous change in n_s and n_d which would yield nearly the same R_0 . Third, the change in the Hall coefficient may be due to a combination of changes in the magnetic moment and in the effective number of carriers accompanying a 4*f*→5*d* shift. Evidence for the second possibility is that the high temperature limit of the upper branch of the curve seems to be about the same as the high temperature (180°K) limit of the lower branch.

The increase at low temperatures along the lower branch of the loop may be the result of the extraordinary effect. It has been suggested²⁴ that the transition to the condensed state may be incomplete, and if this were true then there might be an extraordinary effect in the noncondensed phase (which is probably h.c.p.) causing the rise.

The value of the Hall coefficient at 180°K on the lower branch, which is assumed to be the ordinary coefficient R_0 , because there seems to be little or no temperature dependence there, corresponds in the one-band model to 1.6 holes per atom effective in conduction. This result assumes an increase in density of 18 percent associated with the transition to the condensed state. Although the work here indicates that the

²⁴ Parkinson, Simon, and Spedding, Proc. Roy. Soc. (London) A207, 137 (1951).

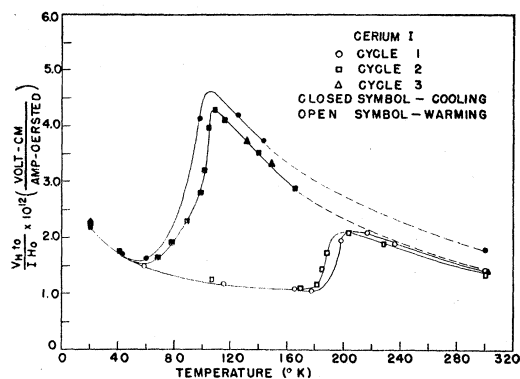


FIG. 6. Hall coefficient of cerium as a function of temperature.

transition may be incomplete at that temperature, these values for the change in density and linear dimension were taken from the x-ray structure findings of Schuch and Sturdivant⁶ which were carried out at 78°K.

D. Praseodymium

The Hall effect in praseodymium metal was positive at all temperatures studied, and the Hall voltage was linear with applied field to 5600 oersteds at 20.3°K, 78°K, and 300°K. The room temperature value of the Hall coefficient was found to be $+0.709 \pm 0.008 \times 10^{-12}$ volt-cm/amp-oersted. This value was not affected by annealing or cooling within the limits of probable error shown.

X-ray crystallographic analysis resulted in h.c.p. lines of incorrect intensity distribution and in extra lines which could not be indexed as either h.c.p. or f.c.c.

The temperature variation of the Hall coefficient is shown in Fig. 7. Investigation of the magnetic properties of praseodymium¹² have indicated a paramagnetic Curie point at 0°K. The increase in the magnitude of the Hall coefficient below 100°K could be associated with an increasing extraordinary Hall effect as a Curie point at 0°K is approached.

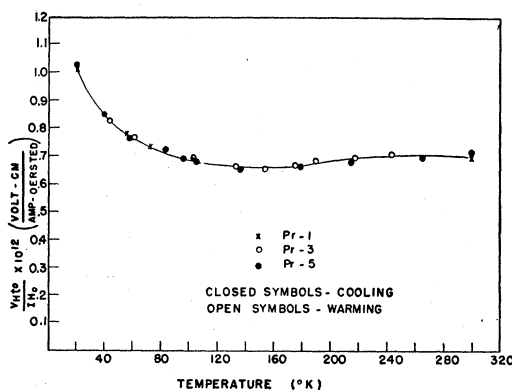


FIG. 7. Hall coefficient of praseodymium as a function of temperature.

The room temperature value corresponds to a contribution to conduction of 3 holes per atom on the basis of a simple one-band model.

E. Neodymium

The room temperature value of the Hall coefficient for neodymium was found to be $+0.971 \pm 0.006 \times 10^{-12}$ volt-cm/amp-oersted. This corresponds in the one-band model to 2.1 holes per atom effectively contributing to conduction.

Figure 8 shows the Hall coefficient as a function of temperature. The small maximum at 70°K may be associated with a magnetic effect. It has been reported¹³ that an extrapolation of magnetic susceptibility data to temperatures lower than those at which measurements were made indicates a paramagnetic Curie temperature at about 70°K, which is approximately the position of the first minimum in the Hall coefficient. Although no magnetic data exists below 80°K, it is also possible that the rapid rise below 40°K could be associated with the extraordinary effect as a paramagnetic Curie point is approached.

F. Gadolinium

The Hall effect in gadolinium was studied from 30°C to 350°C. These measurements were made with the sample in a vacuum furnace. At all the temperatures indicated, the Hall voltage was proportional to the applied magnetic field H_0 , the maximum value of which was 5600 oersteds. According to published data on the magnetic properties above the Curie point,¹³ the demagnetizing field was less than 10 percent of the applied field at temperatures above 80°C. The value of the Hall coefficient V_{Ht_0}/IH_0 at 350°C is -4.48×10^{-12} volt-cm/amp-oersted. The increase as the temperature is lowered might be attributed to the extraordinary effect in a paramagnetic region.

Using the magnetic data of Trombe,¹³ one obtains from Eq. (3) a calculated curve which fits fairly well the experimental curve (Fig. 9) for temperatures above 120°C if one takes $R_0 = -0.95 \times 10^{-12}$ volt-cm/amp-oersted and $\alpha = 240$. The calculated values are indicated

by the crosses on Fig. 9. The dotted curve is the curve calculated using $R_0 = -0.4 \times 10^{-12}$ volt-cm/amp-oersted and $\alpha = 600$. At lower temperatures, the calculated curve falls below the experimental curve, indicating that α is increasing as the temperature is lowered toward the Curie point, if one assumes R_0 constant. One can see that this is not a precise way to determine R_0 and α .

The value -0.95×10^{-12} volt-cm/amp-oersted for the ordinary Hall coefficient corresponds in the one-band analysis to 2.1 negative carriers per atom.

G. Dysprosium

The Hall coefficient V_{Ht_0}/IH_0 for dysprosium metal is shown in Fig. 10 plotted as a function of temperature. The effect was negative in the temperature range from 290°K to about 130°K but reversed sign and became positive at lower temperatures. The increase in magnitude followed by the decrease and reversal of sign is believed due to the extraordinary Hall effect. It has been reported that the magnetic susceptibility of dysprosium exhibits a maximum at about 180°K.¹⁴ This may be due to the existence of two magnetic states, and one could understand the behavior of the Hall effect if it were assumed that the parameter α is positive in sign for the high temperature (paramagnetic) state and negative for the state which persists below 180°K.

Below 169°K the Hall voltage was not a linear function of the applied field and evidence of remanence appeared, with the Hall voltage forming a hysteresis loop with applied field. The temperature range in which this occurred is indicated by the dotted portion of the curve.

Because of the limited temperature range over which data were taken, it is difficult even to get an estimate of R_0 and α . Assuming both are constant in the high temperature range, and using Eq. (3), the magnetic data of Trombe, and the experimental values at 290°K and 220°K, one finds $R_0 = -1.3 \times 10^{-12}$ volt-cm/amp-oersted, and $\alpha = 18$. Calculated values of V_{Ht_0}/IH_0 for intermediate temperatures, using these values for R_0 and α , do not agree well with the observed ones, due

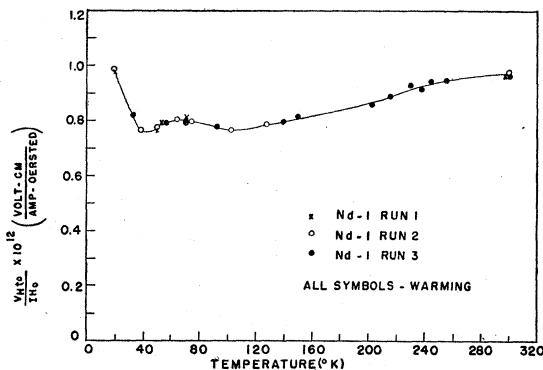


FIG. 8. Hall coefficient of neodymium as a function of temperature.

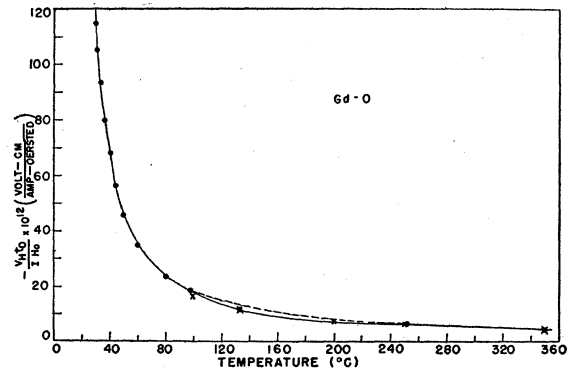


FIG. 9. Hall coefficient of gadolinium as a function of temperature.

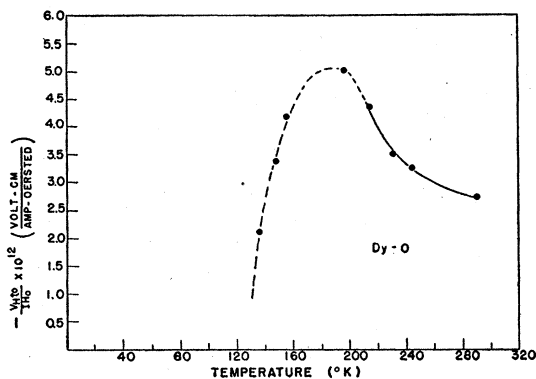


FIG. 10. Hall coefficient of dysprosium as a function of temperature.

possibly to rapid variation of α with temperature in this range.

The number of negative carriers per atom corresponding to $R_0 = -1.3 \times 10^{-12}$ volt-cm/amp-oersted is 1.5 in the one-band model.

H. Erbium

The Hall effect in erbium was negative in the temperature range from 100 $^{\circ}$ K to 300 $^{\circ}$ K and at 78 $^{\circ}$ K and at 20.3 $^{\circ}$ K. The temperature variation of the Hall coefficient V_{H0}/IH_0 is shown in Fig. 11. The increasing magnitude as the temperature decreases appears to be that resulting from the extraordinary effect near a Curie point.

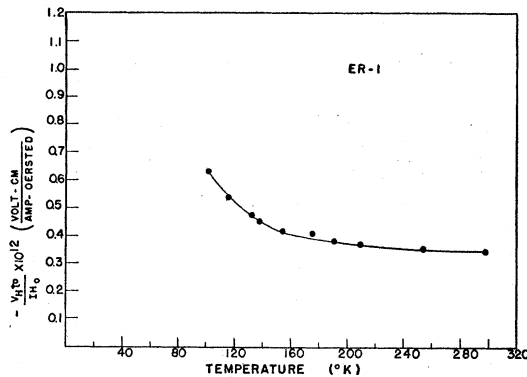


FIG. 11. Hall coefficient of erbium as a function of temperature.

Since the curve is nearly flat at room temperature, the value at this temperature is very nearly R_0 . The room temperature Hall coefficient, -0.341×10^{-12} volt-cm/amp-oersted, corresponds to 2.1 negative carriers per atom in the one-band treatment.

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