Extraordinary Hall-Effect Measurements on Ni, Some Ni Alloys, and Ferrites*†

JEROME M. LAVINE
Research Division, Raytheon Company, Waltham, Massachusetts
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Extraordinary Hall-effect measurements over a wide range of temperature are reported for 99.9 Ni, 99.4 Ni, 95 Ni, several 80% Ni alloys, Fe_3O_4, and $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$. The resistivity ρ of all samples over the same temperature range is also reported. At high temperatures, the extraordinary Hall coefficient R_1 for 99.9 Ni is proportional to ρ^2 as predicted by theory. However, the dependence upon ρ is smaller in the 99.9 Ni sample at lower temperatures and in the samples with higher impurity concentration at all temperatures. The 80% Ni samples exhibit positive R_1, while R_1 in the high-concentration Ni samples is negative. R_1 for both ferrites is negative below about 400°C and positive above this temperature.

The theoretical work on metals generally indicates that R_1 is proportional to ρ^2 and the constant of proportionality r is weakly temperature dependent and of the order of unity. In the high-concentration Ni samples r is negative, of the order of unity, and exhibits a significant temperature dependence at low temperatures. In the 80% Ni samples, r is positive and of the order of 10^{-2}. At room temperature, r is of the order of 10^{-3} in Fe_3O_4 and of the order of 10^{-6} in $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$. In both ferrites, r is strongly temperature dependent. The change of sign of r with temperature observed in both ferrites has not been previously observed in metals or alloys.

I. INTRODUCTION

THE Hall effect in ferromagnets was first measured by Hall[1] in 1881. In 1910, Smith[2] showed that the Hall voltage was proportional to the magnetization, and in 1929, Smith and Sears[3] separated the Hall voltage into two components, one proportional to the magnetization M and the second proportional to the H field inside the sample. The next important contribution appeared in 1950 when Pugh *et al.*[4] showed that the component proportional to the H field yielded the ordinary Hall coefficient R_0. However, efforts to show that the extraordinary Hall component, proportional to the magnetization, was a consequence of an internal effective field acting on the conduction electrons failed because of the impossibly large fields required.

In 1954, Karplus and Luttinger[5] advanced the theory that the extraordinary Hall effect was the result of the spin-orbit interaction of polarized conduction electrons. Subsequently, Smit[6] pointed out that Karplus and Luttinger had not properly taken scattering into account. Smit then proposed[7] a model in which the asymmetric scattering of conduction electrons by impurities, due to spin-orbit interactions, yielded an extraordinary Hall current. Recently, Strachan and Murray[8] performed a calculation using conventional transport theory in which the effect of spin-orbit coupling on each electron was considered and scattering was taken into account by means of a collision time. The noteworthy results of these theoretical works are: (1) Spin-orbit interactions can provide a mechanism with the correc order of magnitude, and (2) as suggested by Karplus and Luttinger, most of the temperature dependence of the extraordinary Hall coefficient R_1 in metals arises from the inclusion of the square of the resistivity as a consequence of the way in which R_1 is defined.

In this paper, extraordinary Hall measurements on a class of materials not previously measured (ferrites), on Ni of somewhat higher purity than previously measured, and on several Ni alloys are reported.

II. EXPERIMENTAL PROCEDURE

The measurements were made at 1 kc/sec employing a dc magnetic field. The equipment previously described[9] was designed to measure the ordinary Hall coefficient in these materials and therefore provided more than adequate sensitivity and resolution.

In a retangular specimen of thickness t, with length-to-width ratio[10] greater than 4, the Hall voltage in ferromagnets is given by

$$V_H=(R_0H+R_1M)I/t, \tag{1}$$

where H is the field inside the sample, M is the magnetization of the sample, and I is the current. By extrapolating the slope of the V_H, H curve above technical saturation (where $M=M_s$ and is essentially constant) to zero field, the value of R_1 is obtained.

In order to compare experiment with theory, the contribution of the effective field acting on the conduction electrons, given by $2\pi(1+p)M_s$, must be subtracted. Wannier[11] has estimated p to be very nearly zero and we shall so regard it. Therefore, the Hall voltage above saturation is

$$V_H=\{R_0(H+2\pi M_s)+R_1'M_s\}I/t, \tag{2}$$

where the extraordinary Hall coefficient is now desig-

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† Supported by the Office of Naval Research.
[1] E. H. Hall, Phil. Mag. **12**, 157 (1881).
[2] A. W. Smith, Phys. Rev. **30**, 1 (1910).
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[6] J. Smit, Physica **21**, 877 (1955).
[7] J. Smit, Physica **24**, 39 (1958).
[8] C. Strachan and A. M. Murray, Proc. Phys. Soc. (London) **73**, 433 (1959).
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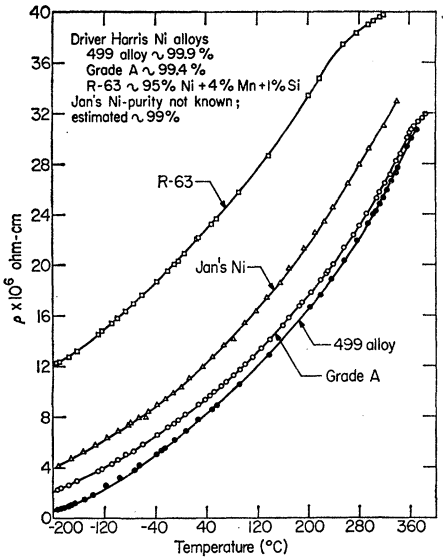

FIG. 1. The resistivity of four samples, 99.9 Ni to 95.0 Ni, from liquid air temperature to the Curie temperature.

nated R_1', and

$$R_1' = R_1 - 2\pi R_0. \tag{3}$$

In most cases, $2\pi R_0 \ll R_1$ and R_1' and R_1 are indistinguishable. We shall therefore omit the prime, noting that corrections to R_1 have been made when $2\pi R_0$ is more than a few percent of R_1.

Values of the saturation magnetization M_s for 499 alloy (99.9 Ni) and Grade A Ni (99.4) were obtained from the 0°K value (M_0) given by Bozorth[12] and a universal curve of M_s/M_0 as a function of T/T_c reported by Jan.[13] The values of M_0 for R-63 alloy (95 Ni-4 Mn-1 Si), Supermalloy (79 Ni-5 Mo-0.5 Mn-15 Fe), and Mumetal (77 Ni-5 Cu-2 Cr-16 Fe) were obtained from Bozorth.[14] The value for Hymu 80 (79 Ni-4 Mo-17 Fe) was obtained from the Carpenter Steel Company. The temperature dependence of M_s for these alloys was likewise obtained from the universal curve for Ni. Since the universal curves of Ni and Fe are very nearly coincident at small values of T/T_c, this procedure introduces little error between liquid air temperature and room temperature. Values of T_c were obtained with good accuracy from measured resistivity-temperature data. In the case of Fe_3O_4, M_s was obtained from Pauthenet's[15] data on a natural crystal. For $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$, M_0 was obtained from the sum of $\frac{1}{4}M_0$ for Fe_3O_4 and $\frac{3}{4}M_0$ for $NiOFe_2O_3$, both obtained from Pauthenet. This procedure is somewhat justified by the fact that the net magnetization of these ferrites is given by the spin of the bivalent metal ion plus a very small orbital contribution. The temperature dependence of M_s was calculated in the same manner. This procedure is probably

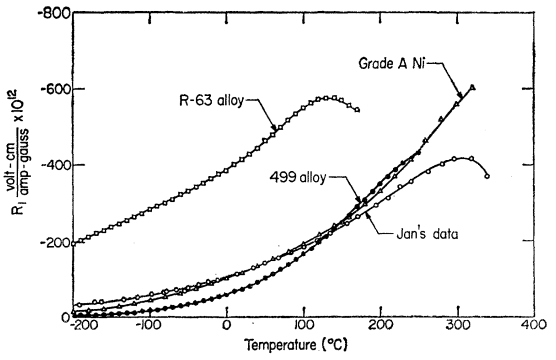

FIG. 3. R_1 as a function of ρ for the high-concentration Ni samples.

FIG. 2. The extraordinary Hall coefficient of high-concentration Ni samples between liquid air temperature and the Curie temperature.

less justifiable, since the exchange interactions which determine the temperature dependence probably do not average in this manner. However, the Curie temperatures of $NiOFe_2O_3$ and Fe_3O_4 are separated by only 25°C.

The resistivity of all samples was measured using a four-contact arrangement and the same measurement system. Values of $r = R_1/\rho^2$ have been calculated from these data.

No data are reported near the Curie temperature where the magnetic field dependence of M_s introduces appreciable uncertainty in R_1. At all other temperatures, the error in R_1 and r from all sources has been calculated[16] to be less than 5% for all samples.

[12] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951), p. 270.
[13] J. P. Jan, Helv. Phys. Acta **25**, 677 (1952).
[14] R. M. Bozorth, see reference 12, p. 317 and p. 870.
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[16] J. M. Lavine, Tech. Rept. 225, Cruft Laboratory, Harvard University, March 10, 1956 (unpublished).

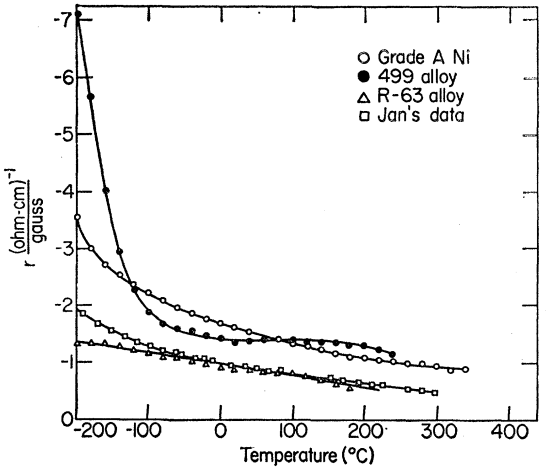

FIG. 4. r as a function of temperature for the high-concentration Ni samples.

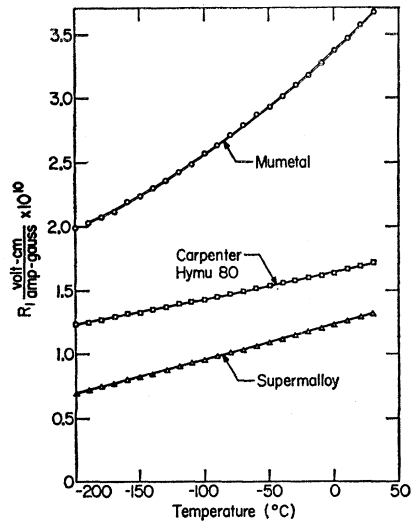

FIG. 6. R_1 of the 80% Ni samples as a function of temperature.

III. RESULTS

A. High-Concentration Ni Alloys

Figure 1 shows the resistivity of four samples ranging from 99.9 Ni to 95.0 Ni from liquid air temperature to the Curie temperature. The shapes of the curves are similar, being displaced by a residual resistance due to the impurity concentration. Figure 2 shows the extraordinary Hall coefficient over the same temperature range. At −195°C, the absolute values of R_1 for 499 alloy and Grade A Ni are roughly $\frac{1}{10}$ and $\frac{1}{2}$ the value observed by Jan.[13] On the other hand, R_1 for R-63 is about seven times larger than Jan's value at this temperature and 65 times larger than R_1 for 499 alloy. At temperatures of the order of 150°C, R_1 for the three highest concentrations Ni samples is roughly the same, while that for R-63 is about three times larger. Figure 3 shows a plot of log R_1 as a function of log ρ. At the high end of the temperature range, the purest Ni shows a $\rho^{1.97}$ dependence very nearly equal to that predicted by theory. However, at the lowest temperatures measured, the same sample exhibits a nearly linear dependence upon ρ. Figure 4 shows a plot of r as a function of temperature for these samples. As the purity of the Ni increases, the temperature dependence of r below room temperature also increases.

B. Alloys ~80% Ni

Figure 5 shows a plot of the resistivity as a function of temperature for Carpenter Hymu 80, Mumetal and Supermalloy. These alloys exhibit small variation of resistivity between liquid air temperature and their Curie temperatures. Figure 6 shows R_1 between liquid air and room temperatures. R_1 varies less than a factor of 2 over this temperature range. However, R_1 in these alloys is positive, while R_1 in the high-concentration Ni samples is negative. Figure 7 shows that r for these alloys is relatively temperature independent over the range of measurement, and in absolute magnitude about 100 times smaller than r for Ni.

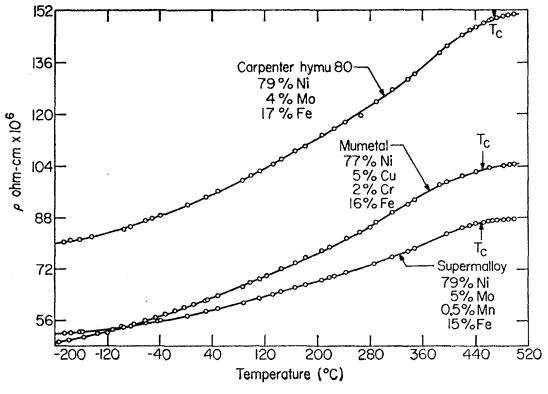

FIG. 5. The resistivity of Supermalloy, Mumetal, and Carpenter Hymu 80 as a function of temperature.

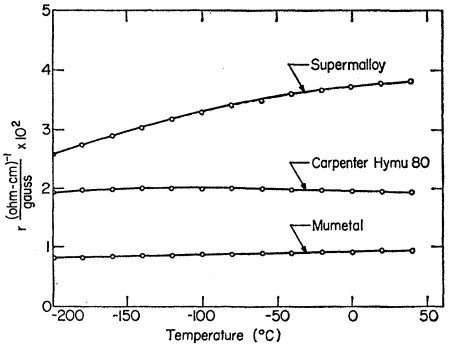

FIG. 7. r as a function of temperature for the 80% Ni samples.

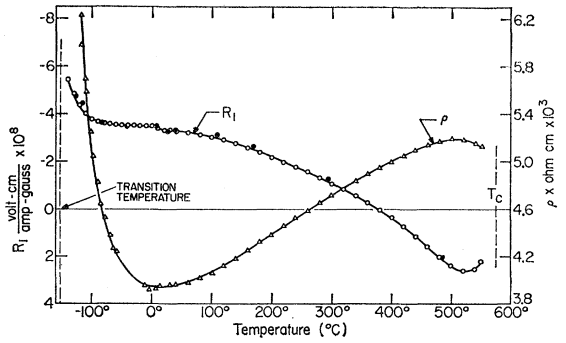

FIG. 8. R_1 and ρ as a function of temperature for Fe_3O_4.

C. Fe_3O_4 and $(NiO)_{0.75}(FeO)_{0.25}Fe_2O_3$

Fe_3O_4 in the region between its transition temperature (−153.8°C) and room temperature exhibits a negative temperature coefficient of resistivity. Between room temperature and about 100°C below T_c it displays a metal-like coefficient of resistivity. Figure 8 shows a plot of the resistivity of Fe_3O_4 obtained from Calhoun[17] (below room temperature) and Smith[18] (above room temperature) on synthetic single crystals obtained from the same source.[19] Values of R_1 are also shown in Fig. 8 for comparison. R_1 at room temperature is negative and roughly 300 times larger than R_1 for 499 alloy. Above room temperature, R_1 decreases in magnitude and goes to zero at 380°C. Above 380°C, R_1 is positive. Below room temperature, R_1 is essentially constant between 0°C and −60°C and increases in magnitude with decrease of temperature to −140°C. The solid data points of Fig. 8 were obtained on a second sample of Fe_3O_4 from the same melt, which was somewhat less homogeneous electrically because of grain boundaries. Between −140°C and liquid O_2 temperature, the absolute value of R_1 increases by a factor of 500, while the resistivity increases by 10^5. Between liquid O_2 and liquid N_2 temperatures, R_1 remains essentially constant, while the resistivity increases by a factor of 7.

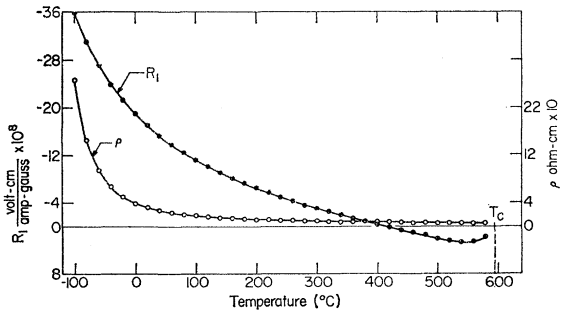

FIG. 9. R_1 and ρ as a function of temperature for $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$.

[17] B. P. Calhoun, Phys. Rev. **94**, 1577 (1954).
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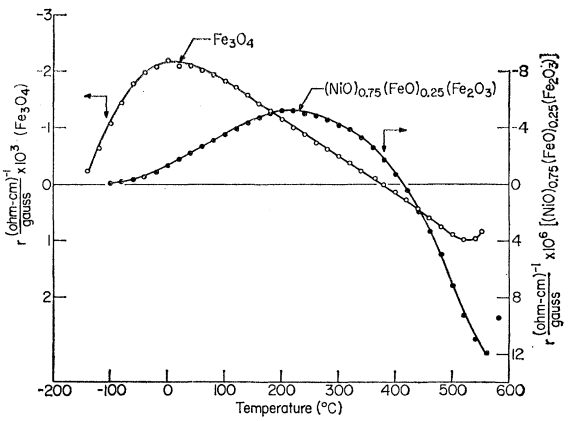

FIG. 10. r as a function of temperature for Fe_3O_4 and $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$.

Figure 9 shows a plot of R_1 and ρ between −100°C and T_c for a single crystal of $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$. At room temperature, R_1 is negative and 5 times larger than R_1 in Fe_3O_4 and 1500 times larger than R_1 in Ni. R_1 decreases in magnitude with increase of temperature somewhat in the same manner as R_1 in Fe_3O_4 and passes through zero at 410°C. Above 410°C, the sign of R_1 is positive.

In Fig. 10 are plotted values of r for both ferrite samples. At room temperature r for Fe_3O_4 is about 10^3 times the value of r for $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$ and 10^{-3} times the value of r for Ni. At liquid air temperature, r for Fe_3O_4 is roughly 10^{-10} times smaller than r for Ni.

In Table I are listed the 300°K values of R_1 and ρ measured on all samples and other pertinent data.

IV. DISCUSSION

According to Karplus and Luttinger, R_1 is proportional to ρ^2 and the constant of proportionality r is only weakly sensitive to temperature and impurity concentration. In their model, interband scattering of d electrons as a consequence of spin-orbit interactions is primarily responsible for the extraordinary Hall current. Previous measurements[13,20] on Fe and the present measurements on 99.9 Ni at high temperatures exhibit a ρ^2 dependence. However, the dependence upon ρ is smaller in the 99.9 Ni sample at lower temperatures and in the samples with higher impurity concentrations at all temperatures. Figure 4 shows that the dependence of r upon temperature is most significant at low temperatures where little change in the population of the d bands is expected. Moreover, the temperature dependence at low temperatures decreases with increasing impurity concentration. The magnitude of r decreases by about a factor of 2 with 5% impurity concentration, and by a factor of 100 with 20% impurity concentration. Moreover, r and R_1 are positive in the 80% Ni alloys. Karplus

[20] C. Kooi, Phys. Rev. **95**, 843 (1954).

TABLE I. Values of M_s, R_1, ρ, r, and R_0 at 300°K and M_0 and T_c for all samples.

Material and composition	M_0 (gauss)	T_c (°K)	M_s (gauss)	R_1 (volt-cm/amp-gauss)	ρ ohm-cm	r (ohm-cm)$^{-1}$/gauss	R_0 (volt-cm/amp-oersted)
499 Alloy, 99.9 Ni	508.8	631	474.7	-7.92×10^{-11}	7.68×10^{-6}	-1.36	-6.02×10^{-13}
Grade A Ni, 99.4 Ni	508.8	631	474.7	-1.23×10^{-10}	8.89×10^{-6}	-1.57	-6.02×10^{-13}
R-63 Alloy, 95 Ni-4 Mn-1 Si	552	519	491.4	-4.23×10^{-10}	2.20×10^{-5}	-8.75×10^{-1}	...
Supermalloy, 79 Ni-5 Mo-0.5 Mn-15 Fe	661.8	723	628.8	1.32×10^{-10}	5.87×10^{-5}	3.81×10^{-2}	(-2×10^{-12})[a]
Mumetal, 77 Ni-5 Cu-2 Cr-16 Fe	545.1	725	517.9	3.63×10^{-10}	6.21×10^{-5}	9.43×10^{-2}	(-2×10^{-12})[a]
Carpenter Hymu 80, 79 Ni-4 Mo-17 Fe	635.3	743	604.0	1.71×10^{-10}	9.42×10^{-5}	1.93×10^{-2}	(-2×10^{-12})[a]
Magnetite, Fe_3O_4	510	847	472.3	-3.28×10^{-8}	3.96×10^{-3}	-2.09×10^{-3}	(-1.80×10^{-11})[b]
Nickel-iron ferrite, $(NiO)_{0.75}(FeO)_{0.25}(Fe_2O_3)$	338	870	308	-1.64×10^{-7}	2.94×10^{-1}	-1.89×10^{-6}	-1.40×10^{-10}

[a] Estimated value.
[b] Upper limit, see reference 21.

and Luttinger have provided no explanation for the positive sign of R_1 in Fe contrasted with the negative sign in Ni.

Smit has suggested that Karplus and Luttinger's results are spurious, arguing that their effect is exactly compensated by the opposite action of the collisons of the electrons with the perturbing potentials due to imperfections, in the stationary state. In his model, Smit proposes that the asymmetric scattering of the d electrons by impurities present in the lattice provides the major contribution to the extraordinary Hall current. Thus a strong dependence upon impurity concentration is provided. However, lattice scattering also contributes, and at temperatures above the Debye temperature he predicts a ρ^2 dependence. Smit has also speculated that impurities with larger or smaller atomic number than Ni would provide attractive or repulsive scattering potentials within the Ni lattice and result in extraordinary Hall currents of opposite sign. This was not borne[7] out by his experiments.

Strachan and Murray have included the effect of s electrons as well as d electrons and conclude that R_1 increases with temperature somewhat more rapidly than ρ^2. Their calculation [Eq. (50)] indicates that R_1 is proportional to ρ^2/M_s with two factors. One of these involves the temperature directly and increases by a factor of 4 between 78°K and 600°K. The second involves the square of a screened nuclear charge. Using the measured values of R_1 for 499 alloy and Grade A Ni, this term must decrease by a factor greater than 10 over the same temperature range in order to fit the data.

None of these calculations are presumed to apply to the ferrites whose conductivity mechanism is at present poorly understood. The magnitude of r in both ferrites is markedly smaller than that observed in both the Ni and 80% Ni alloys and both exhibit reasonably large temperature variation. The sign reversal with temperature observed in both ferrite samples around 400°C has not previously been observed in metals. However, change of sign has been observed with alloying concentration. For example, Smit reports[6] that the addition of about 25% Co or 15% Fe to Ni results in a positive value of R_1 as in pure Co and Fe. The possibility that the sign of the dominant carrier in the ferrites may change at 400°C is discounted because thermoelectric voltage measurements[21] in Fe_3O_4 provide contrary evidence. Moreover, there appears to be no correlation between the signs of R_0 and R_1 in metals. Although R_0 and R_1 are both negative in Ni and positive in Fe, Foner[22] has observed that in Co (at room temperature) R_1 is positive and R_0 is negative. Similarly, Foner has observed that between 70% Ni in Co and 100% Co, R_1 is positive and R_0 is negative.

It is generally concluded that spin-orbit interactions can provide a force of proper magnitude, related to the magnetization capable of yielding the extraordinary Hall current. As pointed out by Strachan and Murray, quantitative evaluations of the details of the electronic wave functions make demands on theory which can only be inadequately met at present. Hopefully, careful measurements on better samples, perhaps even single crystals, with close attention paid to impurity type and concentration, over a wide range of temperatures along with information about the conductivity carrier and possibly the magnetic anisotropy may yield useful information.

ACKNOWLEDGMENTS

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[21] J. M. Lavine, Phys. Rev. **114**, 482 (1959).
[22] S. Foner, Phys. Rev. **91**, 20 (1953).