Hall Effects of the Cobalt Nickel Alloys and of Armco Iron*†

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Experimental investigations of the Hall effects in cobalt, the cobalt-nickel alloys, and Armco iron are described in detail. Precision measurements were made with magnetic fields up to 30 kilogauss in order to separate the ordinary and extraordinary effects. The ordinary effect in all the Co-Ni alloys was found to be negative and agreed within a factor of two with values expected from only 4*s* band conductivity. The ordinary effect in Armco iron was positive indicating hole conduction in the 3*d* band. The field parameter α was observed to be small and negative for most of the cobalt rich alloys, while it was positive for the nickel rich alloys and Armco iron. The limitations in the use of the simple two-band model for explaining the data are outlined. No explanation of α is given.

A. INTRODUCTION

IT has been shown by Stoner[1] that the number of 4*s* electrons/atom in Cu-Ni alloys at 0°K can be estimated from the saturation magnetization M_s, by using a simple band model. This simple band model has been extrapolated to Ni and Co and the Co-Ni alloys. Since it fits a large amount of magnetic data,[2] it has been widely accepted.[3] It is generally supposed that the 4*s* electrons in these metals are solely responsible for their electrical conductivity. Since ordinary Hall coefficients depend upon the number of conduction carriers, Hall measurements should check these predictions. One should expect fair agreement with measurements made at temperatures well below the Curie points of these metals.

Early Hall measurements on Fe, Co, and Ni, which were necessarily made at rather low magnetic fields, disagreed in order of magnitude with the predictions of this simple band picture and gave positive coefficients for Fe and Co. When the conduction is primarily electronic, negative coefficients are expected.

The work of Pugh and Lippert[4] on a number of ferromagnetic elements and alloys suggested that these discrepancies were attributable to internal magnetic fields, proportional to the intensity of magnetization, which were much larger than the measured fields. Studies of old data on nickel[5] indicated that if sufficient precision were available at high fields an ordinary Hall effect could be separated from the extraordinary low field value, previously reported. The ordinary coefficients obtained from these studies agreed reasonably well with the predictions of the simple band theory.

Recent measurements on Cu, Ni, and the Cu-Ni alloys[6] and on a nickel ferrite[7] have confirmed the earlier evidence[5] that the Hall potential difference E_H in ferromagnetic materials may be represented by the empirical formula

$$E_H = (H + 4\pi\alpha M) R_0 I/t, \tag{1}$$

where H = the magnetizing field, M = the intensity of magnetization, α = the field parameter, I = the total current in the rectangular plate sample, and t = the thickness of the sample.

If only the 4*s* band contributes to the conduction and if this band is nearly empty, the ordinary Hall coefficient, R_0, is given by

$$R_0 = -1/N n_s e c, \tag{2}$$

where n_s = the number of 4*s* electrons/atom, N = the number of atoms/cc, and e and c are the electronic charge[8] and velocity of light, respectively. The measurements of Schindler and Pugh[6] on Cu, Ni, and their alloys showed that n_s from Eq. (2) agreed with the predictions of the simple band model to within a factor of 2. However, there were marked deviations from the expected values. For example, there was a large decrease in R_0 at Ni, which could be explained by assuming that there was some 3*d* band conduction.

Assuming that both the 3*d* band and 4*s* band contribute to the conduction, R_0 for the simple two-band model is given by

$$R_0 = -\left\{\left(\frac{\sigma_s}{\sigma}\right)^2 \frac{1}{n_s} \pm \left(\frac{\sigma_d}{\sigma}\right)^2 \frac{1}{n_d}\right\} \Big/ Nec, \tag{3}$$

where n_d is either the number of holes/atom in a nearly filled 3*d* band or the number of electrons/atom in a nearly empty 3*d* band; the minus sign being chosen with the former and the plus sign with the latter. The

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[1] E. C. Stoner, Phil. Mag. **15**, 1018 (1933).

[2] J. C. Slater, J. Appl. Phys. **8**, 385 (1937).

[3] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 434–436; R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), pp. 434–442.

[4] E. M. Pugh, Phys. Rev. **36**, 1503 (1930); E. M. Pugh and T. W. Lippert, Phys. Rev. **42**, 709 (1932).

[5] Pugh, Rostoker, and Schindler, Phys. Rev. **80**, 688 (1950); N. Rostoker and E. Pugh, Phys. Rev. **82**, 125 (1951).

[6] A. I. Schindler and E. M. Pugh, Phys. Rev. **89**, 295 (1953).

[7] Simon Foner, Phys. Rev. **88**, 955 (1952).

[8] By convention, R_0 is defined as negative for electronic conduction, as in copper. Here the quantity e is the absolute value of the electronic charge.

total conductivity is designated by σ, and the conductivities of the 4*s* and 3*d* bands are designated by σ_s and σ_d, respectively. The coefficient R_0 approaches zero as hole conduction increases and would become positive, according to Eq. (3), when $\sigma_d^2/n_d > \sigma_s^2/n_s$. This explanation for the small negative value of R_0 in the nickel-rich Cu-Ni alloys seemed plausible because of the early work which suggested that the sign of the Hall effect in both Co and Fe was opposite to that in Ni and Cu.

The values obtained for R_0 in the Cu-Ni alloy series indicated that such measurements could give some insight into the electronic configurations in this transition group of elements and their alloys. Measurements needed to be extended through the Ni-Co alloys to Co and to Fe. However, to study these metals, it was necessary to employ larger magnetic fields and greater precision in measurements than had been available for the study of the Cu-Ni series of alloys.

B. MEASUREMENT PROCEDURE

For these measurements high sensitivity is important. The magnitude of E_H in Eq. (1) can be increased by decreasing t, but uncertainties in the determination of t decrease the accuracy when t is made too small. The samples[9] used, unless otherwise stated, were machined from cast ingots to 4.5 cm×2 cm×0.1 cm, annealed at 800°C in helium for two hours, then slowly cooled to room temperature. The sample holder was similar to that of Schindler and Pugh,[6] but pressure contacts between the sample and current electrodes were used.

In making Hall measurements on nonmagnetic materials with high resistivity, a number of systematic errors are eliminated or reduced[10] by using alternating currents and by reversing the magnetic field. However, with ferromagnetic metals, these procedures introduce more difficulties than they cure. For example, an alternating sample current induces stray potentials. This limits the sample current that can be employed profitably and thus reduces the accuracy of the measurements. Furthermore, it is difficult to attain with ac measurements the sensitivity of 2×10^{-9} volt attained here with the dc system. Therefore, a dc system has been adopted for these measurements.

A diagram of the measuring system is shown in Fig. 1. The appropriate potential (either from *c* and R_1, for the Hall emf, or from the appropriate thermocouple, for the Ettingshausen correction measurements) is fed to the Wenner potentiometer, 2, where it is balanced to the nearest 10^{-7} volt. The remaining difference potential ($<10^{-7}$ volt) is amplified by the breaker amplifier, 3,

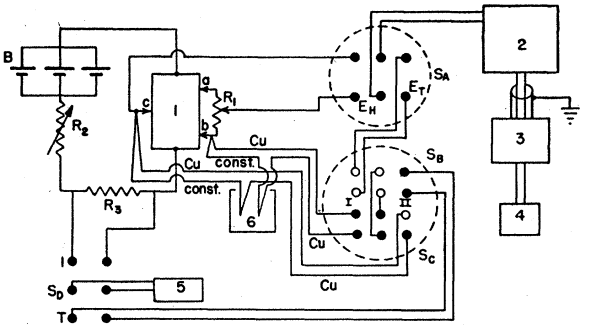

FIG. 1. Schematic diagram of dc measuring circuit: 1—sample, 2—Wenner potentiometer, 3—Liston-Folb model 10 breaker amplifier, 4—Esterline-Angus recorder, 5—portable Rubicon potentiometer, 6—ice bath; *a*, *b*, and *c*—copper probes (*a* and *b* are 4 mm apart), R_1—1Ω Micropot voltage divider, R_2—variable resistor, R_3—150-amp, 50-mv shunt, *B*—degaussing batteries, S_A, S_B, S_C—oil immersed switches.

and recorded by 4. This amplifier-recorder system is calibrated by making 10^{-7} volt changes with the Wenner potentiometer at short time intervals. Both the sample current and the temperature were measured while recording the Hall effect. In order to attain the desired sensitivity, complete electrical and thermal shielding was needed. Great care was required to avoid electrical leakage between the various elements, including the ground. Induced voltages in the measuring circuit caused by vibration or small magnetic field variations were reduced by rigidly mounting the lead wires in positions that minimized the effect of unavoidable loops in the measuring circuit. With these necessary precautions, a sensitivity of $\pm2\times10^{-9}$ volt was obtained.

The sample was mounted in the 1 in. gap between iron-cobalt poles of a new A. D. Little magnet. These poles were truncated cones, tapered from 11 in. diameter to $5\frac{3}{4}$ in. diameter. The magnetic field could be changed rapidly and reproducibly (1 part in 8000) in predetermined steps or reversed in direction by a current control system described elsewhere.[11] The field was uniform to 0.5 percent or better over a 1-in. diameter (covering the central region of the sample) for the fields used in this work. A small flux coil, mounted on the sample, in conjunction with a sensitive galvanometer arranged as a flux meter, was used to measure *B*.

Thermal stability was attained by turning on the sample current and magnet cooling system for about two hours before making measurements. A number of effects can produce temperature variations within the sample. The more important ones are the slow thermal drift of the magnet and the sample current supply system, hysteresis losses within the sample caused by changing the magnetic field, the magnetocaloric effect, and the Ettingshausen effect. The copper probes and the sample constituted a thermocouple so that any temperature variation within the sample superimposed

[9] The impurities in cobalt in percent by weight as analyzed by Westinghouse Research Laboratory are 0.52 Ni, 0.16 Fe, 0.04 Cu, 0.12 C, 0.07 Mn, and 0.01 S. The impurities in percent by weight in nickel as analyzed by the International Nickel Company were 0.12 Cu and 0.23 Co. The Armco iron was not analyzed but the nominal impurities are given as 0.015 C, 0.035 Mn, 0.025 S, 0.005 P, 0.003 Si, and traces of Cu and Ni. The compositions of the Co-Ni alloys were known to within 1 percent.

[10] E. M. Pell and R. L. Sproull, Rev. Sci. Instr. **23**, 548 (1952); J. J. Donoghue and W. P. Eatherly, Rev. Sci. Instr. **22**, 513 (1951).

[11] S. Foner, thesis, Carnegie Institute of Technology, June, 1952 (unpublished).

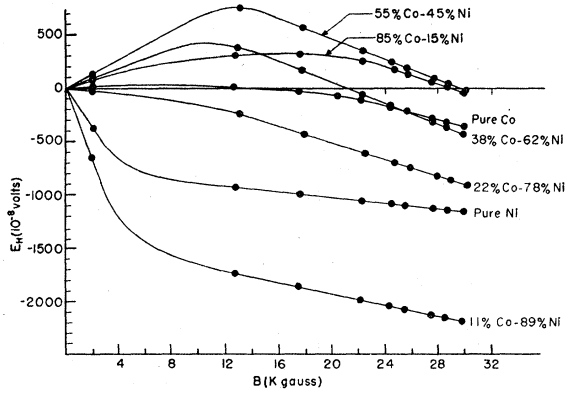

FIG. 2. Hall potential difference *versus* magnetic induction for the Co-Ni series of alloys normalized to $I=25.0$ amp, $t=0.1$ cm for temperatures from 9 to 13°C.

potentials on the Hall potential. The emf's caused by small thermal drifts were eliminated by observing the change in potential for incremental field changes and subtracting the potential drift (quite small) from the field dependent contributions. Using the copper constantan thermocouples (Fig. 1), the field dependent temperature variation at the probes (such as the Ettingshausen effect) could be measured to about 3×10^{-4}°C in spite of a fairly large thermal drift. If the Ettingshausen temperature change is measured with field reversals (at various fields) the magnetocaloric effect (already suppressed to a large extent by the thermal conduction of the current leads) is eliminated, since it does not reverse with field direction. The Ettingshausen correction for R_0 was less than 1 percent for all the metals studied, except Ni for which 2 percent correction was made. The Ettingshausen correction for α was 0.1 or less.

Nearly adiabatic boundary conditions were imposed by the method of measurement. For metals, it is usually assumed that the heat current, which is conducted along with the primary electric current, does not produce an appreciable temperature gradient along the direction of the primary electric current because of the high thermal conductivity. However, a small temperature gradient along the sample which reversed with reversal of the primary electric current, could be observed by the thermocouples at probes *b* and *c* in Fig. 1, which were placed about 2 mm apart along the length of the sample. The maximum temperature difference between probes *b* and *c* was 0.4°C for some of the Co-Ni alloys but was at least an order of magnitude smaller for pure Co and Armco iron. Calculations showed that the corrections to the Hall effect because of the transverse thermomagnetic effects, resulting from this temperature gradient, were negligible. A detailed consideration of the various electric and thermal effects and their boundary conditions has been given by Sommerfeld and Frank.[12]

[12] A. Sommerfeld and N. H. Frank, Revs. Modern Phys. **3**, 1 (1931).

C. EXPERIMENTAL PROCEDURE FOR REDUCING SYSTEMATIC ERROR

Usually Hall measurements are made by reversing the the applied magnetic field and observing the corresponding changes in potential so that any potentials which do not reverse with reversal of the applied field are experimentally eliminated. In principle such a procedure could be used here. However, with ferromagnetic metals, this procedure introduces several difficulties. Generally, in the ferromagnetic materials, the Hall potential changes rapidly at low fields and much more slowly at fields above saturation. High field data must be examined very accurately to obtain R_0 and α. Thus when the field reversal method is used for these measurements, large potentials are observed which must be subtracted from each other. Large errors are inherent in such procedures. Furthermore, large hysteresis and eddy current losses are encountered in ferromagnetic metals with field reversal, so that extraneous thermal effects are introduced which further limit the precision. Thus, the incremental method of measurement leads to much greater accuracy in R_0, especially, if the small field-dependent potentials which do not reverse with field reversal are eliminated by the procedure described in Sec. *D*.

Because of the small, extraneous potentials which depend on the field but do not reverse with it, the observed incremental potentials are different for different directions of the field; i.e., the observed slope of E_H *vs* B curve at high fields changes slightly when the field is reversed. Fortunately, these extraneous potentials are much less field dependent at high fields than at low fields. The errors caused by these potentials can be eliminated by averaging the ordinates of the curves obtained with the two field directions.

The origin of these small potentials is uncertain. They may be the result of field dependence of the resistivity of the sample (magnetoresistance) or to field dependence of the thermocouple constant of the circuit composed of the copper probes and the sample. While both effects must be present, tests indicate that the magnetoresistance effect is the most important.

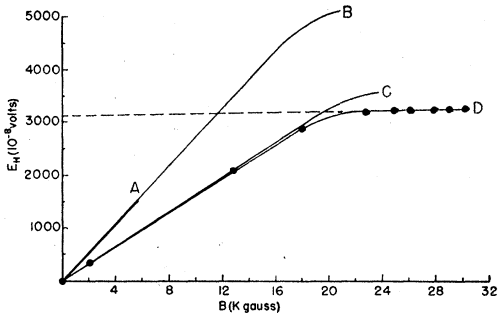

FIG. 3. Hall potential difference *versus* magnetic induction for Armco iron, curve *D* compared with curves *B* and *C* by Smith in 1910 and *A* by Unwin in 1921, all normalized to $I=25.0$ amp, $t=0.1$ cm at room temperatures (curve *D* at 13°C).

In practice, it is not feasible to change R_1 (Fig. 1) during a series of measurements. For this reason R_1 is positioned so that a small bias is applied to the measuring system to prevent drift from reversing the polarity of the potential applied to the potentiometer. This avoids the spurious potentials that would be introduced by a reversing switch in this circuit. Thus this bias depends upon the resistivity of the sample, which in turn depends upon the magnitude but not the direction of the field.

Several experiments were conducted to study this effect. They included reversing the direction of the primary current, changing the setting of R_1, and varying the magnitude and reversing the direction of the magnetic field. The dependence of this effect upon the material of the sample was also investigated. The results of all of these experiments could be satisfactorily explained by assuming a transverse magnetoresistance effect. Two extensive sets of data for the 11 percent Co–89 percent Ni sample were taken, one immediately after the other. The primary current direction was reversed for one of these sets and R_1 was carefully repositioned to obtain identical bias conditions. The positioning of the sample and leads was not disturbed. The two values of R_0 obtained agreed to within 0.1 percent. No difference in magnitude of this extraneous effect at high fields could be detected.

If the effect is attributable to a transverse magnetoresistance, it should be most noticeable near the Curie temperature. To test this, measurements were made on on a sample containing 70 percent Ni–30 percent Cu, whose Curie point is near room temperatures. As expected, the effect was larger than in any of the Co-Ni alloys.

D. EXPERIMENTAL RESULTS

The variations of Hall emf with magnetic induction, B, for a number of Co-Ni alloys, normalized to a current of 25.0 amp and a thickness of 0.100 cm (values near to the experimental ones), are shown in Fig. 2. All of the data presented in this paper were obtained by the following procedure. The changes of Hall emf with incremental changes in field were arithmetically averaged for three or more runs. The same procedure was then used for the field in the reverse direction and the results for the two field directions were averaged algebraically to obtain the experimental points. In this way, any potentials which did not reverse with field direction were eliminated. The differences in the slopes of the E_H *vs* B curves for opposite field directions above magnetic saturation were less than 1 percent for all the metals except Ni.

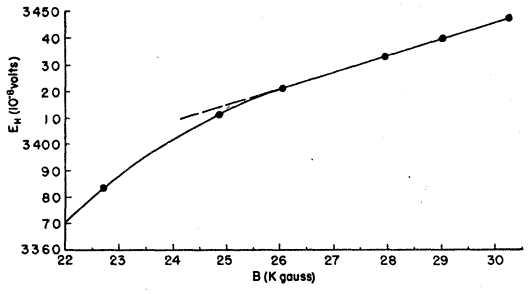

FIG. 4. Hall potential difference *versus* magnetic induction for Armco iron, showing the high field part of curve D in Fig. 3.

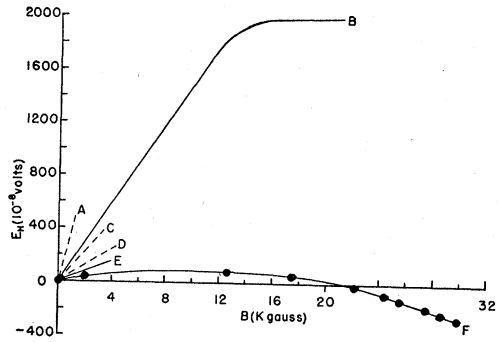

FIG. 5. Hall potential difference *versus* magnetic induction for cobalt at room temperature. Curves A and C by Ettingshausen and Nernst (1886), B by Smith (1910), D by Unwin (1921), and E by Zahn (1904), are compared with the new data F, all normalized to $I=25.0$ amp and $t=0.1$ cm.

The origin of coordinates for each of the E_H *vs* B curves was determined by observing the change in Hall emf for field reversals at some field well above magnetic saturation. The curves above saturation were straight lines within the accuracy of measurement for all of the ferromagnetic metals investigated.

No previous Hall data are available for the Co-Ni alloys, though early results on the elements Ni, Fe, and Co are available. The new data on Ni, shown in Fig. 2, agree well with older experiments at low fields and extend the results to higher fields.

The new data on Armco iron are shown by curve D in Fig. 3. Early results on iron also are plotted in Fig. 3 for comparison. Curve A[13] (which extends only to 6.3 kilogauss) and B[14] are not in good agreement with curves C[14] and D. This may be explained by the higher purity of the iron used in C and D. The high field portion of curve D is shown in Fig. 4. It is interesting to note that the iron was obviously not saturated below 26 kilogauss.

The rather large spread of the early low field data for cobalt is shown by the comparisons in Fig. 5. Unfortunately, the values of magnetic induction used in the early experiments are not available for curves A, C, or D. Curve E extends only to 4 kilogauss. The initial slopes of the curves in Fig. 5 are all positive, which explains why positive Hall coefficients for cobalt are found in the early literature. However, the new data taken up to high fields as shown by curve F in Fig. 5 demonstrates that the ordinary Hall coefficient

[13] F. Unwin, Proc. Roy. Soc. (Edinburgh) **41**, 44 (1921).
[14] A. W. Smith, Phys. Rev. **30**, 1 (1910).

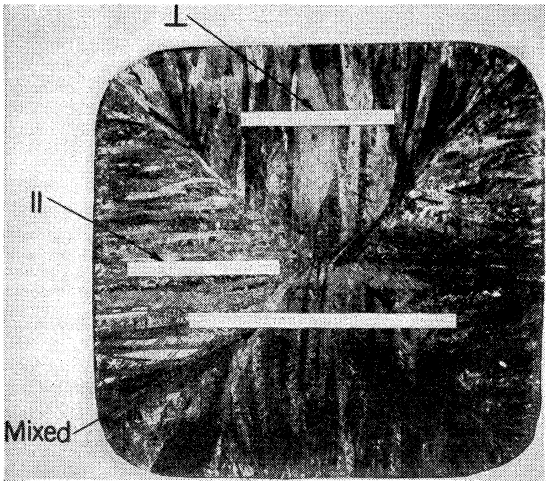

FIG. 6. Cross section of columnar cobalt ingot, etched to show the relative positions of samples used for the Hall effect measurements that are plotted in Fig. 7.

is negative in cobalt, a fact which certainly is not apparent from curve B.

The large discrepancies between the curves in Fig. 5 suggested the possibility that Hall effects in cobalt may be structure sensitive. When the cobalt ingot from which the sample was cut was etched and photomicrographed, the pronounced columnar structure shown in Fig. 6 was revealed. X-ray analysis of an unannealed section of this ingot indicated the presence of both cubic and hexagonal cobalt. Because of the sluggish phase transformation that takes place around 300°C, such mixtures are fairly common in cobalt. The direction perpendicular to the columnar axis was the (100) direction in the f.c.c. phase and the (10·1) direction in the h.c.p. phase. If the Hall effects are strongly structure sensitive, Hall measurements might be expected to vary with the orientation of the columnar axis. Accordingly, two differently oriented samples (designated ⊥ and ||, depending on the direction of the columnar axis with respect to the face of the sample) were cut from this ingot as shown in Fig. 6. The location from which the original sample was cut is indicated by the designation "mixed" in Fig. 6. While the original sample was annealed before the Hall measurements were made, the two new samples were left unannealed to preserve their orientations. The Hall measurements made on these three samples[15] at fields above 12 kilogauss are plotted in Fig. 7. Since the slopes of the three curves are nearly the same at high fields, R_0 is nearly the same for all. The small vertical displacement between the ⊥ and || curves indicate that α is only slightly dependent upon the orientation. The somewhat larger displacement of these two from the curve for the "mixed" crystal is apparently the result of the dependence of α on the state of anneal. Certainly differences in orientation cannot account for the large variations in the Hall effects indicated by the curves shown in Fig. 5.

It appears that the large spread of data in Fig. 5 must be attributed to the variability in the impurity content of the cobalt used. Analysis of the early papers of Ettingshausen and Nernst,[16] Smith,[14] Unwin,[13] and Zahn[17] show that they had great difficulties trying to procure pure cobalt. For example, the curves A and C were measured on two samples of what was believed to be the same material. In a private communication, A. W. Smith states that his Co undoubtedly contained impurities. Unwin and Zahn both attempted to produce electrolytic cobalt. The results of the latter two investigators (curves D and E) agree more closely with the results obtained here for cobalt[9] shown in curve F.

E. ANALYSIS OF DATA AND RESULTS

1. Methods of Analysis

The analysis of the data follows directly from the empirical formula. The Hall constant R may be defined by $R=(t/I)(\partial E_H/\partial B)$, and, from Eq. (1), substituting $H=B-4\pi M$,

$$R=\frac{t}{I}\frac{\partial E_H}{\partial B}=R_0\left[1+4\pi(\alpha-1)\frac{\partial M}{\partial B}\right], \tag{4}$$

so that $R=R_0$ when $\partial M/\partial B=0$ or when $\alpha=1$. Therefore, when the temperature of the ferromagnetic metal is not too close to its Curie point, $\partial M/\partial B$ is so small, at high magnetic fields, that R may be considered equal to R_0. The slope of the straight line portion of the E_H *vs* B curve above saturation then can be used to calculate R_0. When M is a constant equal to M_s at high fields, α may be calculated in two independent

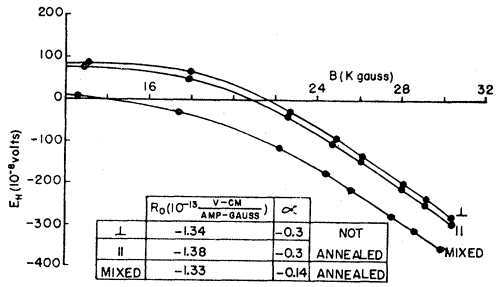

FIG. 7. Hall effect in differently oriented columnar cobalt samples compared with an annealed sample having a mixed orientation, all normalized to $I=25.0$ amp and $t=0.1$ cm at temperatures between 9 and 13°C.

[15] Notice that the temperature for mixed Co in Fig. 7 is lower than for that shown in Fig. 5. A limited range of temperatures from 8 to 25°C was used for these measurements. The absolute magnitude of the initial slope of the E_H *vs* B curves increased slightly with increasing temperature for all the Co-Ni alloys and Armco iron over this range. This temperature dependence agrees with Smith's data below the Curie temperature for iron, cobalt, and nickel and also with data of Lippert and Pugh on 70 percent Fe–30 percent Ni.

[16] H. Zahn, Ann. Physik **14**, 924 (1904), discusses the iron impurities in the samples used by Ettingshausen and Nernst.

[17] H. Zahn, Ann. Physik **14**, 886 (1904).

ways[7] as a test of the applicability of Eq. (1). Extrapolating the high field straight line back to the $B=0$ axis and substituting in Eq. (1), the intercept is $4\pi(\alpha-1)M_sR_0I/t$. Thus, without using the low field data, α can be determined if M_s is known. The second method uses the low field data. Equation (4) may be written as

$$\frac{\partial E_H}{\partial B}=\left[\alpha+(1-\alpha)\frac{1}{\mu}\right]\frac{R_0I}{t}, \tag{5}$$

where μ is the incremental permeability. At low fields $\mu\gg1$ and at high fields $\mu\cong1$, so that the ratio between the low and high field slopes determines α. Thus there are two independent methods for determining α when the E_H *vs* B curve is a straight line at high fields. In general, these two values of α will be equal only if Eq. (1) is applicable and if $\partial M/\partial B$ is negligible at the highest fields employed. Another method of calculating α (equivalent to the first method) is convenient for curves of the type shown in Fig. 8. Using Eq. (1) and extrapolating the straight line portion at high fields to the $E_H=0$ axis, where $B=B_0$,

$$\alpha=1-(B_0/4\pi M_s). \tag{6}$$

For this special type of curve a null detection method[18] can be used for determining α.

2. Verification of the Empirical Formulation

The values of α obtained from the ratio of the low and high field slopes in Fig. 2 are in good agreement with the values for α given in Fig. 9. The low field data were too limited for this to constitute a proof of the validity of Eq. (1), which here is presumed to have been established at low fields by experiments reported

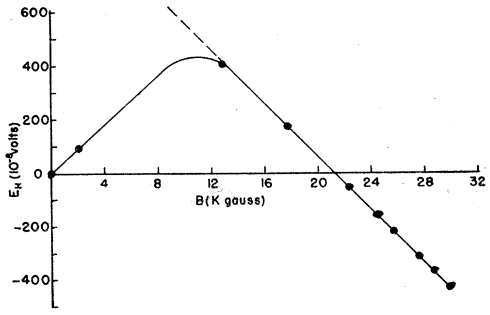

FIG. 8. Hall potential difference *versus* magnetic induction for 38 percent Co in Ni, normalized to $I=25.0$ amp and $t=0.1$ cm at 9°C.

[18] Ferromagnetic metals which show a behavior similar to that in Fig. 8 may be examined quite easily to determine α for the other transverse galvano- and thermomagnetic effects. If Eq. (1) applies to these transverse effects and if $M=M_s$ where the E_H *vs* B curve crosses the B axis, a null detection method can be used to obtain α very simply. By observing the change in the transverse potential or the transverse temperature difference with the reversal of various values of B until a null is obtained, B_0 can be determined. If M_s is known from an independent measurement, Eq. (4) gives the value of α.

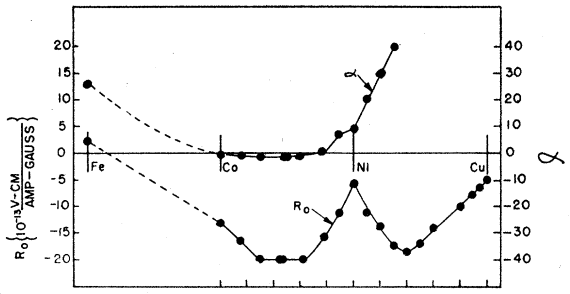

FIG. 9. Values of R_0 and α *vs* composition for elements and binary alloys from Fe to Cu.

previously.[4] A better check was found in the Armco iron data where the slopes could be determined more accurately; the initial slope from Fig. 3 and the final slope from Fig. 4. The value of α obtained from the intercept is 25.6 (using $4\pi M_s=21.6$ kilogauss) while that obtained from the ratio of slopes is 26.2. This excellent agreement indicates that Eq. (1) is valid and that sufficiently high fields were used to accurately determine R_0. Figure 4 illustrates the importance of making measurements at sufficiently high fields, for the E_H *vs* B curve does not become a straight line until 26 kilogauss has been exceeded. The point at 26 kilogauss is actually 4×10^{-9} volt below the straight line while the three points at higher fields deviate by less than 1×10^{-9} volt.

3. Results

The results obtained to date with the ferromagnetic elements and alloys, including those on the previously investigated Cu-Ni alloys,[6] are shown in Fig. 9. The values of R_0 were obtained from high field data assuming $R=R_0$ in Eq. (2). The values for α were obtained by extrapolating the high field straight line portion of the E_H *vs* B curve to the convenient E_H or B axis. Corrections[6] to R_0 should be made for the Cu-Ni alloys between 20 percent and 60 percent Cu because α was large and $\partial M/\partial B$ at room temperatures was not small enough to be neglected, since at room temperatures these alloys were too near to their Curie points. No such corrections were needed for the data on Ni-Co alloys. The Curie temperature of these alloys increases almost linearly from Ni to Co (Ni 358°C, Co 1115°C). Thus with measurements made at room temperatures, these alloys were far below their Curie points and $\partial M/\partial B$ could be neglected at high fields. Furthermore, from Fig. 9, α is quite small for the Co-Ni alloys. The combination of a small $\partial M/\partial B$ and a small α assures that $R=R_0$ to a high accuracy. Although the Curie temperature for Armco iron is high (770°C), its α is so high that a small correction of the order of 3 percent for R_0 would be required if $\partial M/\partial B\sim10^{-4}$. Since no data are available yet for Co-Fe alloys, the lines for α and R_0 are dashed between these two elements.

F. DISCUSSION

1. The Effective Number of Conduction Electrons/atom, n^*

Corrected values of R_0, α, and n^* for all the annealed samples are listed in Table I.

The n^* was calculated from Eq. (2) and is plotted in Fig. 10 along with the number, n_s, of 4s electrons/atom, inferred from magnetic data.[19] The value of n^* for Armco iron is -3.02 (i.e., 3.02 holes). For convenience in plotting Fig. 10 has not been extended to include this point. The data for the Cu-Ni alloys were obtained from the work of Schindler and Pugh.[6] The agreement between n^* and n_s within a factor of two from Cu to Co is as good as that found for most monovalent metals. Compared to the earlier results obtained at low fields for Ni, Co, and Fe, this agreement is remarkable. From this early data n^* was too low in Ni by a factor of 20, of the opposite sign and too low in Co by a factor of 10, and too low in Fe by a factor of 30.

2. The Field Parameter α

At present the quantity α is not well understood. Pugh and Rostoker[20] have recently discussed a number of proposals for explaining this quantity and have shown that none of them appear entirely satisfactory. It appears to be a much more complex quantity than R_0.

If α does represent an effective field term, it should be observed in other conduction phenomena. Smit[21] has used a similar effective field formulation for his low temperature magnetoresistance data on some ferromagnetic metals and finds $\alpha\sim 2$ for Ni and $\alpha\sim 1$ for Fe at liquid nitrogen temperature. This is in good agreement with $\alpha=1.9$ for Ni obtained by Jan and Gijsman[22]

TABLE I. Corrected values of R_0, α, and n^* for the annealed samples.

Composition percent Co in Ni	$R_0\left(10^{-13}\frac{\text{v-cm}}{\text{amp-gauss}}\right)$	α	t(°C)	n^*
0	− 5.6	9.3	9	1.23
11	−11.3	7.3	8	0.61
22	−15.6	0.1	11	0.44
38	−19.9	−1.0	9	0.35
53	−19.6	−1.3	10	0.35
55	−19.5	−1.4	12	0.36
70	−19.6	−1.1	12	0.35
85	−16.4	−0.9	13	0.42
100	−13.3	−0.14	14	0.53
Armco iron	+ 2.45	25.6	13	−3.02

[19] The value of M_s increases almost linearly from Ni to Co so that the number of holes in the d band, n_d, has been presumed to increase in the same manner in this range. Measurements of M_s at $H=11.0$ and 18.0 K oersteds were made for the Co-Ni alloys at room temperature. The results agreed closely with those at $H=10K$ oersteds, reported by O. Bloch, Arch. Sci. Phys. et Nat. **33**, 293 (1912), and are not included here.

[20] E. M. Pugh and N. Rostoker, Revs. Modern Phys. **25**, 151 (1953).

[21] J. Smit, Physica **16**, 612 (1951).

[22] J. P. Jan and H. M. Gijsman, Physica **18**, 339 (1952).

from Hall measurements at this same temperature. They also measured the low field Hall effects for iron at low temperatures and thus determined the product $R_0\alpha$, but they were unable to obtain sufficiently high fields to determine R_0 separately. By using the value of R_0 determined here at room temperatures for Armco iron, an approximate value of α can be calculated from their data. The result, $\alpha=1.3$, is again in good agreement with Smit's value of $\alpha\cong 1$ for Fe. This calculation assumes that in Fe the low temperature R_0 is close to that at room temperature, which may not be valid. For example, Jan and Gijsman found that R_0 in Ni at low temperatures was about half that at room temperature. These limited data do suggest that the effective field $H+4\pi\alpha M$ in Eq. (1) may be the same quantity observed by Smit in his magnetoresistance measurements.

3. Two Band Model

Although the experimentally determined n^* shown in Fig. 10 agrees to within a factor of two with n_s, the deviations are too great to be accounted for by experimental error. The values of n_s plotted in Fig. 10 are taken from the two band model that has been used to account for the saturation magnetization of these metals. If the values of R_0 could be interpreted in terms of band models, Hall measurements would provide considerable information concerning the electronic structure of these bands.

It has been shown[5] that the high value of n^* in Ni can be accounted for by assuming that the 3d band also contributes to the conduction. Schindler and Pugh[6] point out that the low values of n^* they obtained for the alloys containing from 30 percent to 60 percent Cu in Ni should not be taken too seriously, since these alloys were measured[23] at temperatures near to or above their Curie points. Corrections[6] for the fact that $\partial M/\partial B\neq 0$ at high fields are in the right direction to improve the agreement with predicted values.

In comparing values of n^* with those of n_s, it is convenient to proceed to the left in Fig. 10 from 20 percent Cu in Ni toward Co. As Ni is approached the rise in n^* relative to n_s can be attributed to the increased conductivity in the 3d band caused by the increase in the number of holes. The decrease in n^* beyond Ni can then be attributed to the decrease in conductivity in the 3d band because of the decreasing mobility in this band as $\partial^2\epsilon(k)/\partial k^2$ approaches zero. One might then expect that, when n^* goes below n_s beyond 12 percent Co in Ni, the conduction in the 3d band changes to the electronic type. However, small amounts of electronic conduction in the 3d band would make n^* larger rather than smaller than n_s. Actually Eq. (3) will yield values of $n^*<n_s$ only for very large values of σ_d/σ. This becomes clear when Eq. (3) is written in terms of the ratio δ obtained by dividing the

[23] Low temperature measurements on the Cu-Ni alloys are now in progress.

mobility in the 3*d* band by the mobility in the 4*s* band. When $\sigma_d/\sigma_s=\delta n_d/n_s$ is substituted into Eq. (3)

$$n^*=(n_s+\delta n_d)^2/(n_s\pm\delta^2 n_d), \quad (7)$$

where the negative sign applies to conduction by positive carriers and the plus sign applies to conduction by electrons in the 3*d* band. The conduction in the 4*s* band is assumed to be electronic in all cases, since in these metals this band can be considered nearly empty.

From Eq. (7) the value of n^* can be positive and less than n_s only if $\delta\gg1$. When $\delta=1$, $n^*=n_s+n_d$ for electronic 3*d* conduction and $n^*>n_s+n_d$ for positive carrier 3*d* conduction. With Eq. (3) it is very easy to account for values of n^* that are fairly large compared to n_s and impossible to account for values of n^* less than n_s, unless $\delta\gg1$, which seems improbable.

It must be concluded that the two band model, using Eqs. (3) and (7)[24] cannot account for the observed values of R_0 in these metals, with $n_s\geqq0.6$. If n_s could be assumed to be less than 0.35 per atom or could be assumed to decrease monotonically from near 0.6 at 60 percent Cu in Ni to near 0.2 or 0.3 at Fe, the experimental values for R_0 could be explained with the two band model, using Eqs. (3) and (7).

With either of these assumptions the data on R_0 can be explained as follows: The 3*d* band is divided into sub-bands. The top sub-band is filled to the inflexion point near 38 percent Co in Ni. From there on to pure Co the conduction in this 3*d* band becomes electronic as the sub-band is further depleted. Since R_0 is positive in Fe, the contribution to R_0 from the 3*d* band holes exceeds the contribution from the 4*s* electrons. This indicates that the next sub-band is being emptied. One objection to this explanation is that the choice of any value for n_s less than 0.6 makes it difficult to account for the saturation magnetization, unless one assumes some net polarization of the 4*s* electrons.‡

N. Rostoker has suggested that the approximation of a spherical Fermi surface used in these models may be at fault. For example, the value of n^* for copper is about 50 percent too high.[25] Detailed calculations of the band structure by N. Rostoker in collaboration with Walter Kohn are now in progress.

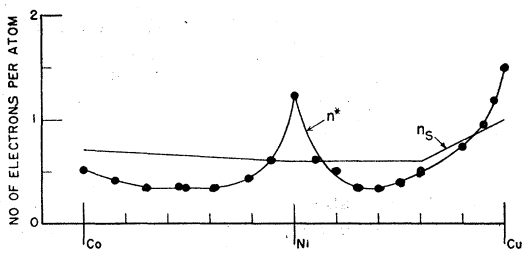

FIG. 10. Effective number of electrons, n^*, *vs* composition for elements and binary alloys from Co to Cu. The generally accepted values of n_s are plotted for comparison.

G. SUMMARY

Room temperature measurements of the ordinary Hall constant, R_0, and the field parameter, α, have been completed on Ni, Co, Fe and the Co-Ni alloy series. The sign of R_0 in Fe indicates conduction by positive carriers (3.0 holes/atom). For all of the other ferromagnetic metals studied here R_0 agrees to within a factor of two with the value predicted from the assumption that all of the conduction is electronic with from 0.6 to 0.7 electron/atom. This agreement is comparable to that of the previous work on Cu-Ni alloys. The detailed behavior of R_0 in these binary alloys from Cu through Ni to Co suggests varying amounts of conduction from the 3*d* band. However, this detailed behavior cannot be explained with a simple two band approximation without making one of two doubtful assumptions. To explain the data with this approximation, it must be assumed either that the mobility in the 3*d* band may be much greater than that in the 4*s* band or that the number of electrons/atom in the 4*s* band may be less than 0.35. Probably this band model is too simple and more exact calculations must be made to account for the data.

We are indebted to N. Rostoker for his very valuable aid and suggestions in numerous discussions and to J. E. Goldman, R. Smoluchowski, W. Kohn, and A. I. Schindler for their comments and criticisms. We are also indebted to R. W. Turner for the x-ray analysis of the columnar cobalt.

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[24] In deriving these equations, it is assumed that the bands are either nearly full or nearly empty. However, this is not a serious limitation if the 4*s* band can be considered nearly empty. The contribution to R_0 from the 3*d* band is relatively small in any case. When the 3*d* band is neither nearly full nor nearly empty (say about half full), its conductivity should be so low as to produce only a small effect.

‡ *Note added in proof.*—It is generally assumed that the *g* value in these ferromagnetic metals and alloys is equal to 2. Recent results of A. J. P. Meyer, Compt. rend. **235**, 1382 (1952) showed a spectroscopic *g* value of 2.20 which was independent of concentration up to 28 percent Cu in Ni. This would decrease the expected value of n_s by only 10 percent.

[25] At copper the 4*s* band is approximately half full. Therefore, the large value of n^* corresponding to a small value for R_0 may be merely evidence that the band cannot be considered nearly empty.

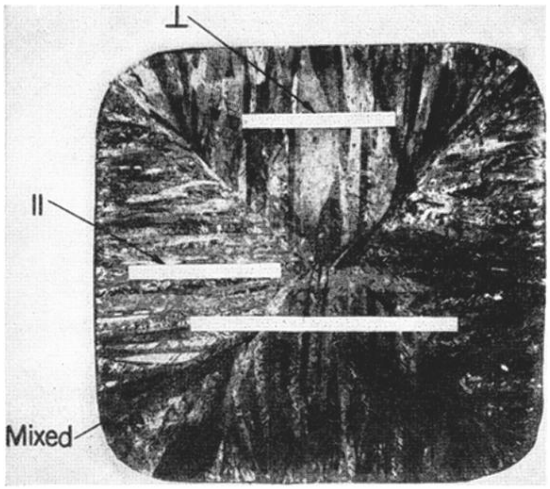

FIG. 6. Cross section of columnar cobalt ingot, etched to show the relative positions of samples used for the Hall effect measurements that are plotted in Fig. 7.