applies, we calculate

$$I=(\alpha/\gamma)(\beta n_0 aU/\varphi k).$$

This means that I is proportional to U and further that I is a function of temperature. Both results agree with the experimental findings (cf. Fig. 11).

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Conduction Electrons in Pseudonickel Alloys from Hall Data*

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The two Hall coefficients and resistivity of four Ni–Cu–Fe alloys having 28 electrons per atom, with Ni content from 97 to 70 atomic percent, have been measured at 20°K, 77°K, and room temperature using fields up to 3.1 webers/meter^2. R_0 is found to increase with decreasing temperature for all compositions, and also to increase with decreasing Ni content for each of the three temperatures measured. The effective number of conduction electrons calculated from the R_0's measured at low temperatures is found to fall smoothly from the anomalous peak at pure Ni to about 0.3 at 70% Ni, in agreement with the predictions of the four-band model. A short summary of the considerable evidence supporting this model is given. The extraordinary Hall coefficient, R_e, is negative at all temperatures for the three samples richest in Ni, being increasingly negative as the Ni content is lowered. On the other hand, the 70% Ni–20% Cu–10% Fe alloy has positive extraordinary Hall coefficients at all temperatures. The behavior of R_e obeys none of the variously proposed theoretical relations.

INTRODUCTION

A BAND model for explaining the ordinary Hall coefficients in alloys of the first transition group of elements has been introduced by Pugh.[1] This model, which was originally proposed by Mott[2] to account for the temperature dependence of the resistivity of Ni, has been singularly successful in predicting the magnitude and temperature dependence of the ordinary Hall coefficients as measured in a considerable number of different alloys.[3–6] The predictions of this band model have been compared chiefly with data obtained in this laboratory, as data obtained in other laboratories is usually too incomplete to make these comparisons. This lack of completeness may be due to magnetic fields that are too small and/or cover too narrow a range for discriminating R_0 from R_1, samples are too thin for accurate measurements, or there is a failure to make measurements over a sufficiently wide range of temperatures.

The need for high accuracy and for covering a wide range of large magnetic fields stems from the fact that R_0 must be obtained from the relatively small slope of the ϵ_H (Hall field per unit sample current density) versus B curve (magnetic induction) at values of B large enough to assure that this slope is a straight line. That is, if M is the magnetization,

$$(\partial\epsilon_H/\partial B)=R_0+(R_1-R_0)(\partial M/\partial B)$$
$$=R_0+R_e(\partial M/\partial B)=R_0^* \text{ by definition.} \quad (1)$$

Thus R_0^*, the slope of the ϵ_H versus B curve, is the same as R_0 only where $R_e(\partial M/\partial B)$ is negligible. Even at very low temperatures, this latter term may be slow to approach negligible values as B is increased. Values for R_0 obtained with fields between 1 and 2 webers/meter^2 (10 to 20 kgauss) are often completely unreliable. Near Curie temperatures, the term $R_e(\partial M/\partial B)$ remains comparable with R_0 to the largest fields obtainable in this laboratory, about 3.2 webers/meter^2.

The alloys of Ni containing about 20 to 50% Cu or 30 to 80% Co have R_0's at temperatures far below their Curie temperature that correspond to approximately 0.3 conduction electron per atom. This agrees with predictions of the band model, since only half of the 4s electrons, the half with spins parallel to the field, have mobilities large enough to affect the measurement. Furthermore, measurements upon the temperature

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‡ Submitted by A. C. Ehrlich in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.
[1] Emerson M. Pugh, Phys. Rev. **97**, 647 (1955).
[2] N. F. Mott, Proc. Roy. Soc. (London) **A153**, 699 (1936).
[3] A. I. Schindler and E. M. Pugh, Phys. Rev. **89**, 295 (1953). S. Foner, F. E. Allison, and E. M. Pugh, *ibid.* **109**, 1129 (1958). F. E. Allison (unpublished data on Ni_3Mn).
[4] S. Foner and E. M. Pugh, Phys. Rev. **91**, 20 (1953).
[5] F. E. Allison and E. M. Pugh, Phys. Rev. **102**, 1281 (1956).
[6] P. Cohen, thesis, Carnegie Institute of Technology, 1955 (unpublished).

dependence of R_0 for these alloys show that the number of conduction electrons per atom approaches 0.6 as the Curie temperature is reached. This was expected, since at the Curie temperature the number of holes in the parallel and antiparallel $3d$ bands become equal, so that mobilities of the two halves of the $4s$-band electrons become equal.

For pure Ni and for Ni-rich alloys with less than 20% impurities, the R_0 measurements cannot be explained as simply. As has been pointed out by both Pugh[1] and Coles,[7] if R_0 depended only upon electronic structure, then it should vary smoothly as the total number of electrons per atom is increased from 27 at pure Co, to 29 at pure Cu. In fact however, measurements show a distinct cusp at pure Ni, and a less pronounced cusp at pure Co, with the magnitude of R_0 being smaller in both Ni and Co than in the alloys.

Pugh[1] assumed that conduction by holes in the $3d$ band was responsible for this anomaly because conduction by holes would produce a Hall emf tending to cancel that produced by the $4s$ electrons. This assumption required that the addition of alloying atoms to pure Ni must reduce mobilities more rapidly for the $3d$ holes than for the $4s$ electrons. A check of the plausibility of these assumptions could be made by measuring R_0's in alloys having the same 28 total electrons per atom as are found in Ni. If the model is valid, the R_0's should be expected to behave in such alloys much like they do in the alloys of Ni-Cu and Ni-Co, i.e., they should have the same type of dependence upon the total impurity content and upon the ratio of their temperatures to the Curie temperature. Furthermore all of these Ni alloys, with as much as 30% impurity content, should have R_0's, measured at temperatures well below their Curie temperatures, that correspond to approximately 0.3 conduction electron per atom.

Some early measurements were made by Smit[8] on such alloys which he called pseudonickels. Although Smit's results were not complete enough to test this hypothesis, they were encouraging. The data obtained in this investigation are sufficiently complete to make the assumptions appear plausible. Four different pseudonickels, consisting of Fe, Ni, and Cu in proportions to give 28 total electrons per atom have been measured at room temperature, at 77 and 20°K.

Theoretical investigations of the origin of R_e, the extraordinary Hall coefficient, have been considerably less successful than those for R_0. The subject has been treated a number of times and stirred some controversy.[8–11] All treatments, however, attribute R_e to a spin-orbit coupling of the $3d$ electrons, and all predict some relation between R_e and a quadratic in the resistivity. The available experimental data have been less than conclusive in support of these theories. We have measured R_e and the resistivity for the four pseudonickels at the same three temperatures as R_0.

EXPERIMENTAL METHODS

The samples used in this investigation were prepared by melting under vacuum the purest available Ni, Cu, and Fe. Ingots of each desired composition were triple-arc melted and cast. They were then cold rolled and machined into samples, probes, and wires. The samples were in the form of flat rectangular plates, nominally 1 cm wide, 10 cm long, and 1 mm thick. Measurements of the length and width were made with micrometers. The thickness was first measured with a micrometer and then remeasured with a profilometer. Due to irregularities on the surfaces and almost imperceptible curvatures of the samples, the more precise profilometer readings were about 5–10% smaller than those obtained with the micrometer. Notwithstanding the care taken, we consider the thickness determination the least accurate of all the quantities measured. Three probes for each of the samples were made from the same ingot as the sample. Two were placed on opposite sides of the sample for measuring the Hall effect and the third about 1 in. from one of the Hall probes for measuring the resistivity. The probes were held in contact with the edges of the sample by means of phosphor bronze springs. Pieces of alloy wire were soldered to each probe, and the junctions of the alloy wires and copper leads were placed inside a copper box to eliminate thermal emf's and any errors due to the Ettingshausen and Righi-Leduc effects. The samples were surrounded by two heavy copper plates to minimize the errors due to the Nernst effect. The density of the samples was measured hydrostatically using carbon disulfide and also by dividing the measured mass by the volume. The two methods agreed to within 1%.

The data were taken at three temperatures. The samples were in direct contact with the baths used, which were liquid hydrogen (20°K), liquid nitrogen (77°K), and a high thermal conductivity silicon oil (room temperature). The sign of the measured potentials was kept constant in spite of the reversal of sign of the Hall potential with magnetic field, by introducing a bias voltage into one Hall-potential lead. This total potential was measured with a Rubicon thermofree potentiometer and a Rubicon photoelectric galvanometer amplifier. The incremental method[4] was used to measure the Hall potential for fields from 8 to 31 kgauss.

In order to determine R_1 it is necessary to know the saturation magnetization per gram, σ. This was measured[12] for samples I, II, and III by the Curie method on powdered specimens of each of the three alloys. The samples were sealed in evacuated tubes and σ was measured at 4 temperatures and extrapolated to find

[7] B. R. Coles, Phys. Rev. **101**, 1254 (1956).
[8] J. Smit, Physica **21**, 877 (1955).
[9] R. Karplus and J. M. Luttinger, Phys. Rev. **95**, 1154 (1954).
[10] J. M. Luttinger, Phys. Rev. **112**, 739 (1958).
[11] J. Smit, Physica **24**, 39 (1958).

[12] Measurements were made by one of the authors in the laboratory of R. R. Heikes of the Westinghouse Research Laboratories with the assistance of R. Mrdjenovich.

the value at 0°K, $\sigma(0°K)$. The value for the fourth sample was arrived at by averaging $\sigma(T°K)/\sigma(0°K)$ for Ni and samples I, II, and III and assumed to be the same as for sample IV. Using the value of $\sigma(300°K)$ given by Bozorth[13] for $H=10$ oersteds, the saturation magnetizations at the other temperatures were calculated.

DATA ANALYSIS

As mentioned in the introduction, care must be taken to distinguish R_0 from the R_0^* at high fields [see Eq. (1)]. We accomplished this by plotting ϵ_H versus B for each set of experimental data. With sufficient accuracy in ϵ_H, the magnitude of B required for saturation could be obtained from visual inspection. Since all of these alloys were saturated as soon as B reached 1.2 webers/meter^2, accurate values for R_0 and R_e could have been obtained with no more than, say 2.2 webers/meter^2 for the maximum magnetic induction.

The Hall coefficients were obtained by a least-squares fitting of the data for the magnetically saturated points to a straight line of the form

$$\epsilon_H = R_0 B + R_e M_s.$$

EXPERIMENTAL RESULTS

Measurements were made on pseudonickel samples containing 3, 7, 14, and 30 atomic % impurities (labeled I, II, III, and IV respectively), where both Cu and Fe are counted as impurities in the nickel. The results are shown in Table I. The values given for M_s at 20°K were obtained by extrapolating the experimental values obtained at 374°, 300°, 193°, and 77°K. It is convenient

TABLE I. Summary of Hall coefficients, resistivity, and magnetic saturation data.

T (°K)	$-R_0\times10^{11}$ (m^3/coul)	$-R_e\times10^{11}$ (m^3/coul)	n^*	$\rho\times10^8$ (ohm m)	$M_s\times10^2$ (weber/m^2)
	97% Ni−2% Cu−1% Fe (Sample I)				
300	7.53	120	0.919	10.6	4.79
77	8.53	16.7	0.811	3.62	5.18
20	9.78	11.9	0.707	2.96	5.21
	93% Ni−4.5% Cu−2.5% Fe (Sample II)				
300	10.5	150	0.655	15.3	4.84
77	14.0	38.9	0.492	6.99	5.23
20	15.3	27.8	0.449	5.79	5.26
	86% Ni−9.3% Cu−4.7% Fe (Sample III)				
300	14.2	205	0.490	23.4	4.49
77	21.9	63.6	0.332	13.6	5.00
20	22.8	54.9	0.306	12.8	5.06
	70% Ni−20% Cu−10% Fe (Sample IV)				
300	18.2	−56.6	0.387	32.8	4.77
77	25.3	−30.2	0.273	18.0	5.15
20	27.2	−29.4	0.259	16.7	5.19

[13] Richard M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951), p. 156.

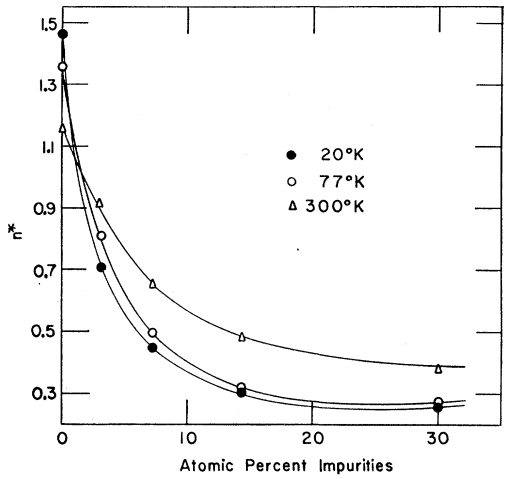

FIG. 1. The effective number of conduction electrons per atom, n^*, for Ni−Cu−Fe alloys containing 28 electrons per atom, plotted against total impurity content, both Cu and Fe being considered as impurities in the Ni. The curves connect values of n^* at the given temperatures for samples differing in impurity content.

to describe the results in terms of n^*, defined as

$$n^* = -1/(R_0 N e),$$

in analogy with the usual relation between R_0 and n for a free electron or single spherical band model.

Curves of n^* as a function of composition for the three measured temperatures are given in Fig. 1. For comparison, we include the nickel data of Dreesen and Pugh.[14] It is interesting to note that n^* for pure Ni increases with decreasing temperature, while the reverse is true for all pseudonickels. As seen in Table I, R_e shows an abrupt change of value and sign in going from the 14- to 30-% impurity sample for all three temperatures.

DISCUSSION (ORDINARY EFFECT)

Smit[8] has made measurements on 7.5- and 15-atomic % impurity pseudonickels (samples II and III) of M, ρ, R_0, and R_e. Our results do not always agree with his nor are they within the limits of the experimental errors. We believe the discrepancies should be ascribed primarily to a combination of two factors. First, we note that Smit's samples were only 0.05 mm thick, making an accurate determination of the thickness very difficult. Second, Smit's measurements were for fields ranging from 0.9 to 1.4 weber/meter^2. This comparatively narrow range could very well cause the usual random errors inherent in the measurements to have an appreciable effect on the values obtained for R_0 and R_e. A much less likely but still possible source of error is the dependence of R_0 on sample thickness. Berlincourt[15] has measured, for pure Cu at 4.2°K, a dependence of R_0 on thickness for samples about 10 times thicker than Smit's. Their resistivity, and therefore the

[14] J. A. Dreesen and E. M. Pugh, Phys. Rev. **120**, 1218 (1960).
[15] T. G. Berlincourt, Phys. Rev. **112**, 381 (1958).

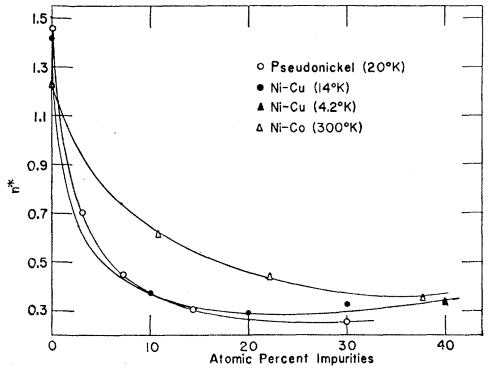

FIG. 2. The effective number of conduction electrons per atom (at the lowest temperatures that have been measured) for Ni—Cu, Ni—Co, and these pseudonickel alloys, plotted against atomic percent of impurities. The curves connect values at the indicated temperatures for samples of differing impurity content. The n^* values for the Ni—Co alloys are high because they have not been measured below room temperature.

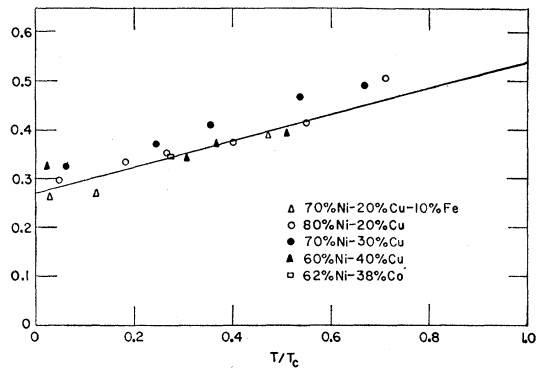

FIG. 3. The effective number of electrons for a number of ferromagnetic Ni alloys plotted against the quotient of the temperature at which they were measured divided by their Curie temperature (T/T_c). The straight line has been drawn on the assumption that 90% of the saturation magnetization is due to the unpaired spins and the remainder to orbital motions. It fits the data fairly well.

reciprocal of the mean-free-path of the electrons, is perhaps two orders of magnitude smaller.

The rather low values of n^* for sample IV at nitrogen and hydrogen temperatures are interesting. If it is assumed that as in Ni there is 0.6 electron per atom in the 4s band divided equally between the parallel and antiparallel sub-bands, then on the basis of the four-band model the lowest possible value for n^* is 0.3. To obtain this it is necessary to neglect completely not only the two d-band conductivities, but also the antiparallel s-band conductivity. The predicted value of n^* could be lowered to 0.27 by attributing a 10-% orbital contribution to the magnetic moment which Beitel and Pugh[16] found necessary to assume in order to explain some Fe-Co data. The remaining discrepancy, about 4%, is approximately within the experimental error. It may also be that one of the approximations used in the band theory (e.g., a relaxation time that depends only on the energy) is not completely valid for these alloys.

In Fig. 2 we have reproduced the hydrogen temperature plot of Fig. 1 and superimposed the Ni-Cu and Ni-Co data of Cohen[6] and Foner and Pugh[4], respectively. The Ni-Cu data were taken at 14°K except for the 40% Cu—60% Ni point, which was at 4.2°K. Helium temperature data are not available for all the alloys of lower Cu content. The Ni-Co measurements are all at room temperatures ($T/T_c \approx \frac{1}{3}$), since these are the lowest temperatures that have been investigated. Smaller values of n^* should be expected for lower temperatures, as is found in the pseudonickels and in the Cu-Ni alloys. In this light the similarity of the three curves, indicative of the near independence of n^* on electron concentration, lends strong support for Pugh's four-band model.

In Fig. 3 we have plotted n^* versus T/T_c, the ratio of the temperature to the Curie temperature, for a number of ferromagnetic Ni alloys. The Cu-Ni data of Allison and Pugh[5] is supplemented for small T/T_c by some of the measurements of Cohen.[6] Included also is our pseudonickel data for sample IV, and a single room temperature measurement on a Co-Ni alloy. All the alloys have sufficiently high impurity content to remove them from the anomalously high values of n^* observed in pure Ni. Data taken for T/T_c greater than 0.7 have not been included, since $(\partial M/\partial B)$ is not negligible for these temperatures.

The experimental data have considerable scatter, particularly the older measurements. Nevertheless there is a clear tendency for n^* to change from about 0.3 to 0.6, as T/T_c increases through 0.7 and is extrapolated to 1.0. A straight line drawn from 0.27 to 0.54, corresponding to an orbital contribution to the magnetic moment of about 10%, fits the data fairly well. Thus the four-band model correctly predicts both the absolute magnitude and the temperature dependence of the relatively high-impurity Ni alloys.

Our four pseudonickel samples give results that are just as predicted on the basis of Pugh's explanation of the cusp in R_0 at pure ferromagnetic metals. However, this explanation should not be considered to have the validity of the more general aspects of the four-band model. The latter has successfully predicted the results of so many experiments that it is hardly open to question. On the other hand, any explanation for the behavior of R_0 in the vicinity of pure Fe, Co, and Ni must still be considered speculative.

DISCUSSION (EXTRAORDINARY EFFECT)

As mentioned above, the interpretation of R_e on the basis of the existing theories has not always been successful. Karplus and Luttinger[9] and Smit,[8,11] both using the spin-orbit mechanism from different points of view, have derived a relation of the form $R_e \propto \rho^2$. For

[16] F. P. Beitel and E. M. Pugh, Phys. Rev. 112, 1516 (1958).

the data given in Table I, there seems to be no general relation between R_e and a power of ρ. For each of the four pseudonickels, however, the points corresponding to the three temperatures do fall on straight lines not passing through the origin, when R_e is plotted against ρ^2. Pure Fe and Fe alloyed with some low percentages of Si obey the relation[17] $R_1=A\rho^{1.9}$. However, there is a deviation from the simple power law at low resistivities which so often occurs.

The treatment of R_e given by Luttinger,[10] based on the theory of electrical transport phenomena of Kohn and Luttinger,[18] gives in addition to a ρ^2 dependence, a linear term in ρ. This theory, which is applicable only to impurity limited resistivity, suggests fitting the data for the 4 samples for a single low temperature with an equation of the form

$$R_e=a+b\rho+c\rho^2.$$

We were unsuccessful in this, as were Dreesen and Pugh[14] and Beitel and Pugh[16] in investigating Ni-Pd and Fe-Co alloys respectively. This is not too surprising in view of the highly simplified model for which the calculations have been carried through.

[17] C. Kooi, Phys. Rev. **95**, 843 (1954).
[18] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

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Energy Transfer within a Spin System*

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The nature of the transfer, within a single nuclear spin system, of energy absorbed from an external source of radio-frequency magnetic field has been investigated by a double-irradiation technique. Energy from a high-power oscillator running at fixed frequency is absorbed by the nuclear spin system. The frequency of a second, low-level oscillator is then swept through the nuclear resonance, sampling the line shape existing in the presence of the strong rf field from the fixed-frequency oscillator. Particular spin systems investigated were the proton system in single crystalline $CaSO_4\cdot 2H_2O$, and the Al^{27} system in aluminum metal. In aluminum, the technique gives direct experimental verification of a completely homogeneous saturation behavior, a behavior expected from elementary considerations. It also gives further verification of the Redfield saturation theory. In $CaSO_4\cdot 2H_2O$, an enhancement effect is observed which allows one to determine the importance of double-flip spin-lattice relaxation processes. The technique could be usefully applied to many spin systems to determine the degree of inhomogeneity in the resonance line broadening.

IN interpreting results of spin resonance experiments, one is often interested in the nature and efficiency of processes by which energy absorbed by part of the spin system from an applied rf magnetic field is shared with the rest of the spin system. The problem is only of interest, of course, when the spectral distribution function of the resonance line, $g(\omega)$, is determined by some mechanism other than lifetime broadening. Knowledge of the nature and efficiency of the energy transfer is crucial in interpreting the results of steady-power magnetic resonance saturation experiments. As a matter of fact, it is often uncertainties about the behavior of this energy transfer which make saturation determinations of T_1, the spin-lattice relaxation time, inferior to direct transient measurements of T_1.

We have applied a double-resonance technique to determine experimentally some facets of the behavior of this energy transfer.[1] Two representative nuclear spin systems have been investigated. One is the proton system in $CaSO_4\cdot 2H_2O$ and the other the Al^{27} system in aluminum metal. The sample is subjected to a fixed-frequency saturating rf magnetic field of amplitude $2H_1$, at frequency ω_1. ω_1 is set at some appropriate position within the frequency spread of the resonance line. We deal entirely with cases in which H_1 is less than the resonance linewidth. Then the frequency of a second, low-level oscillator is swept through the region of the resonance line, and the line shape in the presence of H_1 is measured by this second, tickler oscillator. Details of the experimental arrangement are described in the next section. As a result of this sampling with the second oscillator, we determine the manner in

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[1] Similar double-resonance experiments have been performed by W. A. Anderson, Phys. Rev. **102**, 151 (1956) and by J. Itoh and R. Kusaka, J. Phys. Soc. Japan **14**, 492 (1959).