Two Hall Effects of Iron-Cobalt Alloys*†

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The Hall coefficients and the resistivity of Fe-Co alloys have been measured at 77°K, 169°K, and room temperature using fields up to 3.3 webers/m². For up to 0.2% Co in Fe the ordinary Hall coefficient R_0 is positive at room temperature but becomes negative at low temperatures; for all other compositions R_0 is negative. Analysis with a simple model in which the (4s) conduction band consists of a parallel and an antiparallel sub-band shows that, for up to 20% Fe in Co, the parallel 3d sub-band is filled. It then empties as the Fe content increases, having about 0.2 holes per atom at 50% Fe, but at 65% Fe the bands apparently shift so that again the parallel 3d sub-band is filled. These conclusions remain unchanged if the analysis is based instead upon a model proposed recently in which the 3d electrons may be in nonconducting states as well as in the usual conducting-type states. The extraordinary Hall coefficient R_1 is positive for less than 25% Co in Fe, but for all other compositions it changes from positive to negative as the temperature decreases from 300°K to 169°K. R_1 and the resistivity ρ satisfy the relation $R_1=a+b\rho^2$.

INTRODUCTION

It has been well established that in ferromagnetic materials the Hall effects satisfy the relation

$$Vt/I=R_0\mu_0H+R_1M, \tag{1}$$

where V is the Hall potential, t is the sample thickness, I is the sample current, H is the magnetic field, M is the magnetization, R_0 is the ordinary Hall coefficient, and R_1 is the extraordinary Hall coefficient.[1] Experimentally, R_0 has been shown to correspond to the Hall coefficient for nonferromagnetic materials.[2] Thus, if conduction is due to a single band, R_0 is given by

$$R_0=-1/Nne, \tag{2}$$

where N is the number of atoms per m³, n is the number of conduction electrons per atom, and e is the magnitude of the electronic charge in coulombs.

The Hall effects of the Cu-Ni and Ni-Co alloys have been measured[3-5] at fields high enough that R_0 could be determined accurately. The analysis based upon Eq. (2) with the 4s band assumed to be the only conduction band gave values for n_s, the number of 4s electrons per atom, within a factor of two of those deduced from magnetic data. The differences between the values of n_s obtained from Hall data and from magnetic data as well as the positive values[4,6-8] of R_0 for Fe, Mn, Cr, V, and Ti might be due to hole conduction in the 3d band. However, even on the basis of a two-band model (i.e., 4s electronic and 3d hole conduction) these differences cannot be explained.[9]

A simple four-band model[9] has proved more successful in explaining the discrepancies. The 4s band and the 3d band are each described as being split into two sub-bands with the magnetic moments of the electrons in each sub-band either parallel or antiparallel to the field; the conduction is attributed to the two 4s sub-bands, with different carrier mobilities in the sub-bands due to the difference in the probability of scattering into the unequally filled 3d sub-bands. For this model the expression[9] for the ordinary Hall coefficient reduces to

$$R_0=-(2/Nn_se)[1-2\beta/(1+\beta)^2], \tag{3}$$

where $\beta=\sigma_a/\sigma_p$, σ is the conductivity, and the subscripts a and p refer to the antiparallel and parallel alignment of the magnetic moments, respectively. Allison and Pugh[10] found that Eq. (3) described quite well the temperature dependence of three Cu-Ni alloys from 4°K to well above their Curie temperatures. Thus, apparently a simple model is available for the analysis of Hall data.

Coles and Bitler[11] studied the electronic configurations of the Fe-Co alloys by measuring their saturation moments after various amounts of Al had been added. The Al atoms contribute extra electrons which enter the 3d levels of the transition atoms and change the magnetic moment. The electronic configurations can be deduced from the way in which the magnetic moment per transition atom changes with Al content. In order to study further the electronic configurations in the transition elements, we have measured the ordinary Hall effect at 77°K, 169°K, and room temperature for a number of Fe-Co alloys.

The origin of the extraordinary Hall effect has long

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[1] In this paper quantities are expressed in the rationalized mks system of units in which $B=\mu_0H+M$. The units of B, μ_0H, and M are webers/m², and Hall coefficients are expressed in the unit 10^{-11}m³/coul. In terms of units commonly used: 1 weber/m² = 10^4 gauss, and 10^{-11}m³/coul = 10^{-13}v-cm/amp-gauss.

[2] Pugh, Rostoker, and Schindler, Phys. Rev. **80**, 688 (1950).

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

[4] S. Foner and E. M. Pugh, Phys. Rev. **91**, 20 (1953).

[5] P. Cohen, Office of Naval Research Technical Report, June, 1955 (unpublished); thesis, Carnegie Institute of Technology, 1955 (unpublished).

[6] S. Foner, Phys. Rev. **101**, 1648 (1956).

[7] G. W. Scovil, J. Appl. Phys. **27**, 1196 (1956).

[8] S. Foner, Phys. Rev. **107**, 1513 (1957).

[9] E. M. Pugh, Phys. Rev. **97**, 647 (1955).

[10] F. E. Allison and E. M. Pugh, Phys. Rev. **102**, 1281 (1956).

[11] B. R. Coles and W. R. Bitler, Phil. Mag. **1**, 477 (1956).

been under investigation.[12] In 1954 Karplus and Luttinger[13] derived a relation between R_1 and the resistivity ρ on the basis of the spin-orbit interaction, and similar results have been obtained by other authors.[14,15] (The theory of transport phenomena and, in particular, of the Hall coefficients is now being studied by Luttinger and Kohn.[16]) Since these results were published many investigators have measured both R_1 and ρ, and the agreement between theory and experiment has varied greatly from one material to another. In order to provide more information about the relation between these quantities, we have measured them as functions of temperature for the Fe-Co alloys.

EXPERIMENTAL METHOD

The samples used were homogenized and annealed in hydrogen for a week at 1200°C and then cooled at less than 1°C per minute. They were reheated to 700°C in vacuum, held at that temperature for two hours to remove hydrogen, and again cooled at less than 1°C per minute. This treatment should have produced well-ordered samples[17] which were free of hydrogen.[18]

A sample (a flat plate 2 cm wide, 6 cm long, and 1 mm thick) and wires were made from each alloy. The edges of each sample were then machined to leave four lugs about 0.035 inch wide which protruded about $\frac{1}{16}$ inch from the sample. After the sample was annealed a piece of the alloy wire was spot-welded to each lug; and the junctions of the alloy wires and the copper leads were placed inside a copper box to eliminate thermal emf's and, consequently, any errors due to the Ettingshausen and Righi-Leduc effects. Two of the lugs, on the center line of the sample, were used to measure the Hall potential; the two others, located 2 cm apart on one side of the sample, were used to measure the resistivity. Two thermocouples were clamped independently to the sample about 4.5 cm apart; and the central part of the sample was clamped between two brass sheets (insulated from the sample with mica) to improve rigidity and reduce thermal gradients in the bath.

The high saturation magnetization of the Fe-Co alloys and the (magnetically) unfavorable sample geometry necessitated the use of the A. D. Little magnet[19] with $5\frac{3}{4}$-in. diameter pole pieces and the smallest gap practical ($\frac{5}{8}$ in.). Fields up to 3.3 webers/m^2 were used. To provide for measurements at low temperatures and to thermally isolate the Hall samples at room temperature, a special double-walled brass dewar was used. The cylindrical upper part of the dewar was simply a liquid reservoir. The lower part was rectangular in cross section and fitted into the $\frac{5}{8}$-in. magnet gap; it provided a working space inside approximately 4 in. high and $2\frac{7}{8}$ in. by $\frac{3}{8}$ in. in cross section. The sample was fastened vertically between rigidly mounted current electrodes and was in direct contact with the bath. The baths used were liquid nitrogen (77°K), liquid ethylene (169°K), and a silicone oil with high thermal conductivity (room temperature). Liquid nitrogen boiled off at a rate less than 1 liter/hr while measurements were being made.

A bias voltage was introduced into one Hall-potential lead to offset the reversal in sign of the Hall potential with magnetic field, and the total potential was measured with a Rubicon Thermofree Potentiometer and a Rubicon Photoelectric Galvanometer Amplifier. Since the potentiometer setting can be varied continuously, this is a null system. The incremental method[4,6] was used to measure the Hall potential. One important advantage of this method has not been emphasized; the error in the measured value of R_0 due to the temperature dependence of R_1 is eliminated. If only field reversals were used, a systematic change of 1°C in temperature could lead, in some cases, to an error in R_0 of as much as 2×10^{-11}m^3/coul.

DATA ANALYSIS

If the demagnetizing factor for a flat plate is taken into account, Eq. (1) may be written

$$Vt/I = R_0 B + (R_1 - R_0)M. \tag{4}$$

Usually the plot of Vt/I *versus* B for high B can be represented quite well by a straight line whose slope is R_0^* by definition. By differentiation of Eq. (4), then,

$$R_0^* = R_0 + (R_1 - R_0)\partial M/\partial B. \tag{5}$$

The apparent value of R_1, denoted by R_1^*, is calculated from the high field data using Eq. (4) with $M = M_s$ and $R_0 = R_0^*$.

For the Fe-Co alloys, most of the high-field data could be represented quite well by straight lines. However, just as observed for Armco iron,[4,6] the Hall curves for the 0.1, 0.5, and 15% Co alloys did not saturate even at the highest fields. Thus, according to Eq. (5), $\partial M/\partial B$ was still changing. Consequently, Eqs. (4) and (5) were solved simultaneously for R_0 and R_1, and the magnetic data[20,21] were used to estimate corrections to R_0^* and R_1^* for all the alloys.[22] In most cases the corrections were less than 1%, while otherwise the ordinary Hall coefficients were such that the corrections were not important. Therefore, all corrections have been ignored,

[12] See for example E. M. Pugh and N. Rostoker, Revs. Modern Phys. **25**, 151 (1953).
[13] R. Karplus and J. M. Luttinger, Phys. Rev. **95**, 1154 (1954).
[14] P. N. Argyres, Phys. Rev. **97**, 334 (1955).
[15] J. Smit, Physica **21**, 877 (1955); **24**, 39 (1958).
[16] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957); **109**, 1892 (1958).
[17] W. C. Ellis and E. S. Greiner, Trans. Am. Soc. Metals **29**, 415 (1941).
[18] W. C. Newell, J. Iron Steel Inst. (London) **141**, 243 (1940).
[19] F. Bitter and F. E. Reed, Rev. Sci. Instr. **22**, 171 (1951).
[20] P. Weiss and R. Forrer, Ann. phys. **12**, 279 (1929).
[21] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951).
[22] The effects of the approach to magnetic saturation on the Hall curves and on the measured values of R_0 and R_1 were considered in detail; the results are contained in another paper which has been submitted for publication.

and the values given for R_0 and R_1 in this paper are those usually denoted by R_0^* and R_1^*.

EXPERIMENTAL RESULTS

Measurements were made on Fe-Co alloys containing 0.1, 0.5, 15, 35, 60, 70, 75, 80, 85, and 100% Co. The Hall effects were measured at 77°K, 169°K, and room temperature for values of B between 1.2 and 3.3 webers/m². The values of R_0 and R_1 are shown in Figs. 1 and 2. The results of Foner[4,6,23] and Foner, Allison, and Pugh[24] are also shown in Fig. 1 for comparison. As is usually observed, R_1 is strongly dependent on temperature while R_0 is relatively temperature independent. The resistivity is shown as a function of temperature and composition in Fig. 3. For the mid-range of composition the curves show the well-known minimum due to the ordering which occurs in these alloys.

Attempts to separate the Nernst and Hall effects by the method of Allison and Pugh[10] were unsuccessful. Apparently the Nernst effect is too small in Fe-Co alloys to cause appreciable error in the values measured for R_0 and R_1.

On the basis of the uncertainty in sample dimensions, density, and magnetic field and the errors due to the approach to saturation and random variations from run to run, the values of R_0, R_1, and n^* are known to approximately 3% and the values of ρ to approximately 1.5%.

DISCUSSION

The room temperature values of R_0 for Co and the 0.1% Co in Fe alloy agree quite well with Foner's results for Co and Armco iron, and the values for 50% Co and the 55% Fe-45% Ni Permalloy fall nicely on the curve. The change in sign of R_0 with temperature near Fe is not surprising since small values for R_0 can result from many different electronic configurations, and small changes can easily lead to large changes in

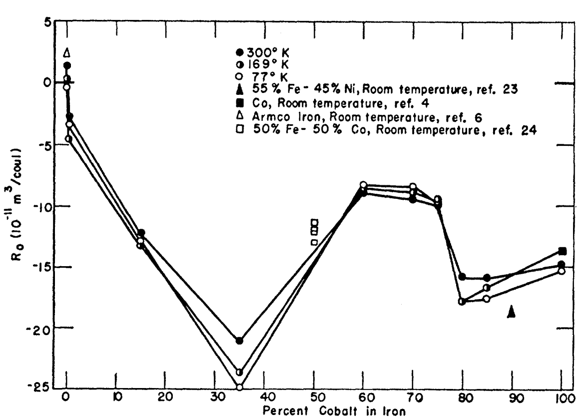

FIG. 1. Ordinary Hall coefficients of the Fe-Co alloys.

[23] S. Foner, Phys. Rev. **99**, 1079 (1955).
[24] Foner, Allison, and Pugh, Phys. Rev. **109**, 1129 (1958).

R_0. Similar behavior has been observed in titanium,[7] in which R_0 changes from -2 at room temperature to $+3$ at 1100°C.

If conduction is due entirely to n_s electrons in two $4s$ sub-bands and if each sub-band contains $n_s/2$ electrons, then the ordinary Hall coefficient is given by Eq. (3). Since the effective number of conduction electrons per atom, n^*, is defined by Eq. (2), it follows from Eq. (3) that

$$1/n^* = (2/n_s)[1-2\beta/(1+\beta)^2]. \quad (6)$$

Mott[25] considered the resistivity of ferromagnetic materials; and, using parabolic $3d$ sub-bands and simple assumptions about the scattering of the $4s$ electrons, derived the relation

$$\beta^3 = N_p/N_a, \quad (7)$$

where N_p and N_a are the numbers of holes per atom in the parallel and antiparallel $3d$ sub-bands, respectively.

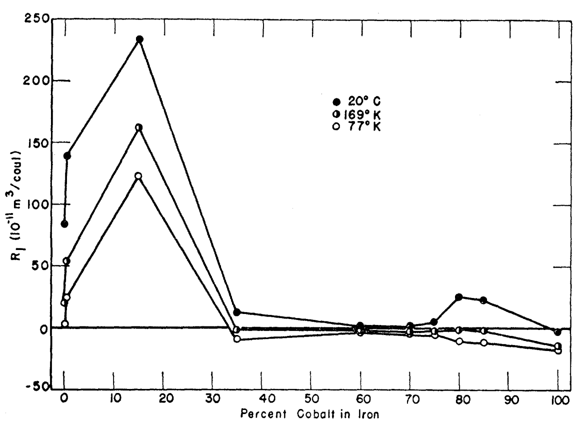

FIG. 2. Extraordinary Hall coefficients of the Fe-Co alloys.

For an alloy in the $3d$-$4s$ transition series the quantities N_a, N_p, n_s, and the effective atomic number Z are related by

$$2N_p = n_s - (N_a - N_p) + (28 - Z). \quad (8)$$

Thus, if n^* and $(N_a - N_p)$ are known from Hall and magnetic data, Eq. (6), (7), and (8) can be solved simultaneously to give n_s, N_p, etc.

Values of n_s and N_p calculated from the Hall data on the assumption that the number of unpaired $3d$ holes per atom, $(N_a - N_p)$, is equal to the number of Bohr magnetons per atom, n_0, are shown in Fig. 4 with the curves Coles and Bitler[11] deduced from magnetic data. The results of calculations made with $N_a - N_p = 0.9n_0$, corresponding to a 10% orbital contribution to the magnetic moment, are also shown. For less than 65% Fe in Co the results agree; one half the $3d$ band is filled for up to 20% Fe, and then holes appear in both $3d$ sub-bands. (The actual number of holes

[25] N. F. Mott, Proc. Roy. Soc. (London) **A153**, 699 (1936).

calculated from the Hall data depends critically upon the band shape assumed.)

For the 35% Co-65% Fe alloy the magnitude of R_0 is so large that, in terms of a band model, the explanation is practically unique.[26] If each unpaired $3d$ electron contributed one Bohr magneton to the magnetic moment, the observed saturation moment of 2.46 Bohr magnetons per atom would require n_s to be at least 0.81. On the other hand, according to Eq. (6), the Hall data indicate a maximum n_s (i.e., $\beta=0$) of $2n^*=0.58$. The discrepancy can be explained by assuming that 10% of the magnetic moment is due to orbital motion. The magnetic data then require only 2.21 unpaired $3d$ holes per atom and a minimum n_s of 0.56. There seems to be no other reasonable explanation of this large value of R_0; apparently the g factor must be taken into account, and one $3d$ sub-band is completely filled. Thus, the Hall data indicate that as the Fe content is increased to 65% the bands suddenly shift so that again one half of the $3d$ band is filled.

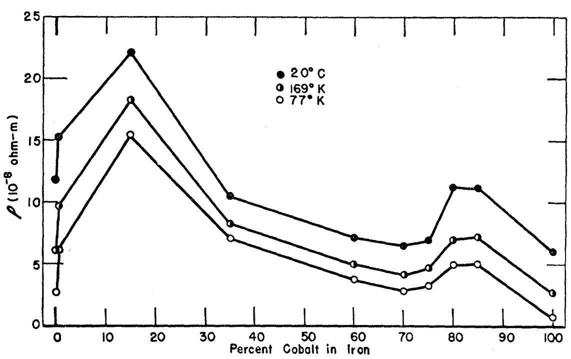

FIG. 3. Resistivities of the Fe-Co alloys.

As is observed near pure Cu and Ni, for less than 35% Co in Fe neither the magnetic data nor the Hall data lead to definite conclusions about the electronic configuration. Coles and Bitler had very few iron-rich alloys so that their magnetic data provide little information about this region, and the positive value of R_0 for Fe could be due to $4s$ hole conduction as well as to $3d$ hole conduction.

Recently Mott and Stevens[27] described a new model for the electronic structure of the transition metals. In the usual description, the $3d$ and $4s$ bands overlap, and electrons in both bands can contribute to conduction. In the new model, the same description applies to the close-packed metals, but in the body-centered metals the $3d$ band is separated into two parts. One part, with a capacity of three electrons of each spin per atom,

[26] In multiple-band models, the larger the magnitude of R_0 the fewer are the combinations of numbers and mobilities of carriers that will lead to a given value of R_0, while the number of combinations leading to a given value of R_0 increases tremendously as the magnitude of R_0 decreases. This behavior was discussed in reference 9.

[27] N. F. Mott and K. W. H. Stevens, Phil. Mag. 2, 1364 (1957).

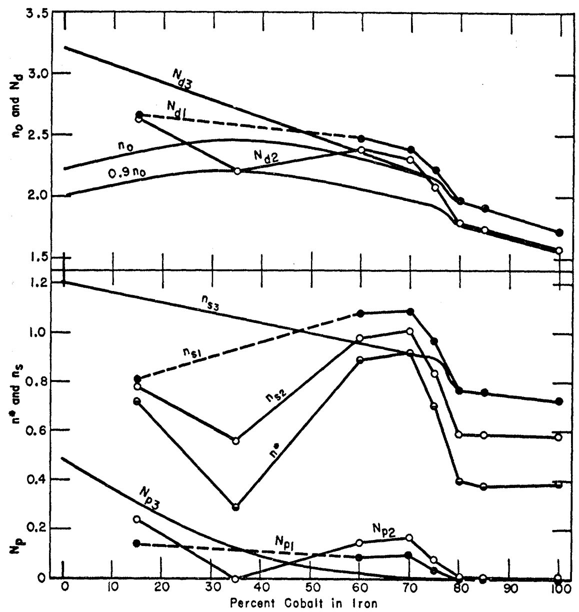

FIG. 4. Saturation moment in Bohr magnetons per atom (n_0), effective number of conduction electrons per atom (n^*), $3d$ holes per atom (N_d), number of holes per atom in the parallel $3d$ sub-band (N_p), and $4s$ electrons per atom (n_s) at absolute zero for the Fe-Co alloys. Solid circles (subscript 1) were calculated assuming the number of unpaired $3d$ holes per atom (N_a-N_p) to be n_0, open circles (subscript 2) were calculated assuming N_a-N_p to be $0.9n_0$, and solid lines (subscript 3) represent values given by Coles and Bitler. At 35% Co, values can be calculated for N_d, n_s, and N_p by assuming N_a-N_p equals $0.9n_0$ but not n_0, as the dashed lines indicate.

corresponds to the usual model; but in the other part, with a capacity of two electrons of each spin per atom, the electrons are in bound states and cannot contribute to conduction. In Fe the nonconducting bands are shifted so that one is completely filled and the other is empty, giving rise to two magnetic electrons per atom. The remainder of the magnetic moment is attributed to magnetization of the conduction electrons.

If the new model is adopted, the relative contributions of the parallel and antiparallel $4s$ electrons can be related in the same way as before to the numbers of holes in the *conducting* $3d$ sub-bands. Further, it is not unreasonable to assume that the $4s$ sub-bands are not shifted and that $3d$ conduction may be neglected. Therefore Eqs. (6), (7), and (8) provide a means of calculating the number of holes in the conducting $3d$ band. The new model leads to results essentially the same as those above, except that the number of $3d$ holes calculated is somewhat smaller.

Spikes appear in the R_0 *versus* composition curve at Fe, Cu, and Ni, as is shown in Fig. 5, though a peak at Co is much smaller and not as sharp. The hump in the curve for the Fe-Co alloys is unique, appearing in the region in which order-disorder transformations are observed. Coles[28] has pointed out that certain features

[28] B. R. Coles, Phys. Rev. 101, 1254 (1956).

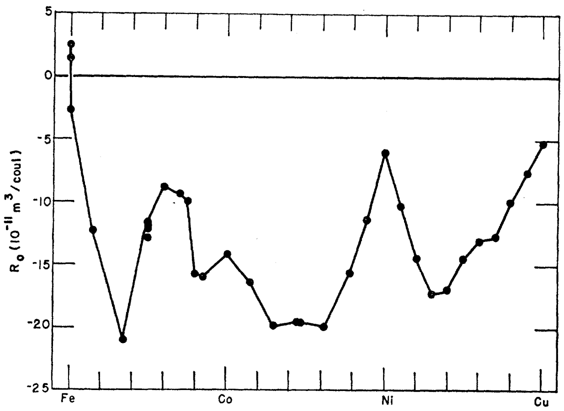

FIG. 5. Ordinary Hall coefficients for Fe-Co, Co-Ni, and Ni-Cu alloys at room temperature.

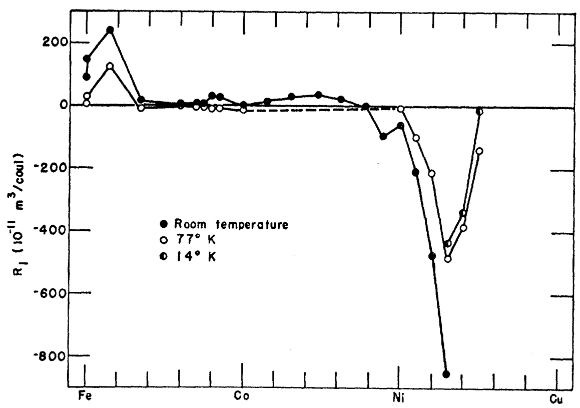

FIG. 6. Extraordinary Hall coefficients for Fe-Co, Co-Ni, and Ni-Cu alloys.

of curves of R_0 *versus* composition, in particular the peaks at pure metals, could be due to changes in the scattering mechanism rather than to changes in the number of carriers. Similarly, the hump in R_0 for the Fe-Co alloys could be attributed to the change in scattering due to the absence of aperiodicity in the lattice. However, examination of Allison's results for the 50% Fe-50% Co samples in various states of order shows that they are predominantly disordered, so that in the completely disordered alloys R_0 apparently would have values corresponding to the "disorder" limit for the 50% alloy rather than the large negative value found for the 35% Co alloy. Thus, although the ordering of the lattice in the Fe-Co alloys might affect R_0 through changes in the scattering mechanism, the hump would seem to be due mostly to shifts in the relative positions of the bands and the corresponding changes in the number and mobility of the conduction electrons.

Figures 2 and 6 show an effect which has not been specifically noted before; R_1 for a given alloy changes sign as the temperature varies. This behavior actually occurred for the 60% Cu-40% Ni alloy measured by Cohen[5] and probably would have been found for the 50% Cu-50% Ni alloy as well if measurements had been made below 14°K. In the Fe-Co alloys dR_1/dT is positive; in the Cu-Ni alloys[5] it is negative. The data for the Co-Ni alloys[4] cover only a small temperature range but indicate that dR_1/dT changes sign at about 20% Co in Ni. The results in Fig. 6 indicate that for a given alloy R_1 is monotonic with temperature, but in some materials[29] dR_1/dT changes sign at low temperatures.

The existing theories for R_1, based upon a spin-orbit interaction, have predicted either $R_1 = A\rho^2$ (references 13 and 14) or $R_1 - R_0 = A\rho^2$ (reference 15). Although a number of authors have found that these relations are approximately satisfied for various materials, the data Fe-Co alloys can satisfy neither relation since R_1 and $(R_1 - R_0)$ both change sign. However, the relation $R_1 = a + b\rho^2$, which includes both theoretical relations, is satisfied quite well for each alloy. The significance of this relation between R_1 and ρ is not known, and certainly it cannot be valid in cases in which R_1 is not monotonic with temperature.

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[29] N. S. Akulov and A. V. Cheremushkina, Zhur. Eksptl. Teoret. i Fiz. 31, 152 (1956) [translation: Soviet Phys. JETP 4, 150 (1957)].