Temperature Dependence of the Hall Coefficients in Some Silver Palladium Alloys*

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The Hall coefficient for Ag—Pd alloys containing 80% and 60% Pd has been measured as a function of temperature from 4°K to 300°K. These alloys are of great interest because their electronic structure is is similar to that of the Cu—Ni alloys, which have been investigated recently. The Hall coefficient has been found to be strongly temperature-dependent in the Ag—Pd alloys; however, the form of the temperature dependence is different from that observed in the ferromagnetic Cu—Ni alloys and is well represented by an empirical equation of the form $R_0^*=A+C/(T-\theta)$. Since the extraordinary Hall effect causes Cu—Ni alloys to exhibit a similar behavior when measured above their Curie temperatures, the temperature dependence in these Pd—Ag alloys is ascribed to an extraordinary Hall effect.

INTRODUCTION

IT has now been well established that the Hall effect in ferromagnetic materials obeys the empirical relation

$$e_H=R_0H+4\pi R_1M, \quad (1)$$

where e_H is the Hall electric field per unit current density, H is the magnetic field, M is the intensity of the magnetization, R_0 is the ordinary Hall coefficient, and R_1 is the extraordinary Hall coefficient.[1,2]

The ordinary effect in a ferromagnetic material corresponds to the Hall effect in a nonferromagnetic material; and consequently, R_0 is the coefficient related to the number of conduction electrons. For a single band, this relation would be

$$R_0=-1/(Nvec), \quad (2)$$

where N is the number of atoms per cm^3, ν is the number of electrons contributed to the conduction band by each atom, e is the magnitude of the electronic charge, and c is the velocity of light. The situation is, of course, complicated in the transition elements by the fact that the s band overlaps a partially filled d band. Even when d-band conduction can be neglected, the value of R_0 depends critically upon the extent to which the two halves of the d band are occupied. Measurements[3] at very low temperatures on Cu-Ni alloys have demonstrated that R_0 is roughly twice as large as those at room temperature, indicating that there can be only 0.3 of an electron per atom sufficiently mobile at these temperatures to influence the Hall effect. A band model[4] based on the ideas of Mott[5] appears to explain the temperature dependence of the Cu-Ni alloys. This model has been carefully checked against recent measurements on three Cu-Ni alloys by comparing the temperature dependence of R_0 with that predicted by the band model.[6] Aside from the expected anomalous behavior in the neighborhood of the Curie temperature, the model is in rather remarkable agreement with experimental results.

In order to test more conclusively the hypothesis that the temperature variation of the Hall coefficient in the ferromagnetic Cu-Ni alloys arises from their ferromagnetic properties, the Hall coefficient of the Ag-Pd alloys have been studied over a similar temperature range. Silver and palladium are the corresponding members of the next transition series, which contains no ferromagnetic elements. It was believed that the temperature variation of the Hall coefficient for the corresponding Ag-Pd alloys would be considerably different from that observed in the Cu-Ni alloys. Experimental results are now available in the range from 4.2°K to room temperature for 80% Pd—20% Ag, and 60% Pd—40% Ag. Although the Hall coefficient is rather strongly temperature dependent in these Ag-Pd alloys, the form of the temperature dependence is different from that of the Cu-Ni alloys. In fact it corresponds to the type of temperature dependence observed in some ferromagnetic transition metals above their Curie temperatures.[7]

EXPERIMENTAL METHOD AND DATA ANALYSIS

The Ag-Pd samples that were used in this investigation were nominally 1 mm thick, 8 mm wide, and were mounted in a holder with 5 cm of the sample left exposed between copper clamps to which the primary current leads were soldered. The main section of the sample holder, which supports both the sample and the probes, was machined from a single piece of 2-in. diameter Micarta. This technique insures that the probes are very nearly perpendicular to the primary current flow.

Measurements at low temperatures were achieved by using liquid baths of helium, hydrogen, nitrogen, ethylene, and propane. The sample temperatures were

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[1] E. M. Pugh and T. W. Lippert, Phys. Rev. 42, 709–710 (1932).
[2] A. I. Schindler and E. M. Pugh, Phys. Rev. 89, 295 (1950).
[3] P. Cohen, Office of Naval Research Technical Report, June, 1955 (unpublished); thesis, Carnegie Institute of Technology, 1955 (unpublished).
[4] E. M. Pugh, Phys. Rev. 97, 647 (1955).
[5] N. F. Mott, Proc. Roy. Soc. (London) A153, 699 (1936).
[6] F. E. Allison and E. M. Pugh, Phys. Rev. 102, 1281 (1956).
[7] Jerome M. Lavine, Office of Naval Research Technical Report No. 225, March 10, 1956, Cruft Laboratory, Harvard University (unpublished).

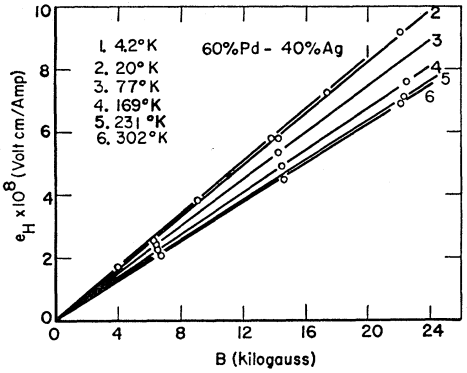

FIG. 1. Hall electric field per unit primary current density *versus* magnetic induction for 60% Pd−40% Ag at various temperatures.

assumed to be equal to the normal boiling points of the liquid baths. Room-temperature measurements were made with the sample submerged in a tube containing a low-viscosity silicone oil.

A two-probe system was used throughout this investigation and the need for a reversing switch was avoided by adding a small bias voltage to one of the Hall potential leads. The Hall potential was measured with a Rubicon Thermofree potentiometer and a Rubicon galvanometer amplifier. Hall-potential measurements were made for reversals in the magnetic field at several different values of the magnetic field. By this method, the Hall electric field per unit current density can be obtained as a function of the magnetic induction and experimental values of the Hall coefficient determined. According to Eq. (1) the ordinary Hall coefficient will be given by $R_0=de_H/dB$ provided the term $4\pi R_1\partial M/\partial B$ can be neglected. Ordinary Hall coefficients determined in this way will be designated by R_0^*; that is,

$$R_0^*=de_H/dB. \tag{3}$$

The Ag-Pd alloys are, of course, nonferromagnetic, and the intensity of magnetization is proportional to the magnetic field; i.e., $M=\chi H$. When this relation is substituted into Eq. (1), one obtains the relation

$$e_H=R_0H+4\pi R_1\chi H. \tag{4}$$

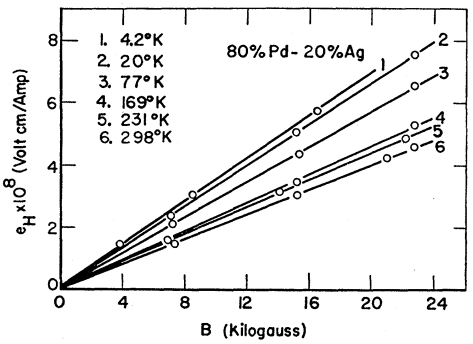

FIG. 2. Hall electric field per unit primary current density *versus* magnetic induction for 80% Pd−20% Ag at various temperatures.

Thus, any extraordinary contribution to the Hall electric field, which is proportional to the intensity of magnetization, will not be separated from the ordinary contributions in a paramagnetic sample.[8]

EXPERIMENTAL RESULTS

The Hall electric field per unit current density was measured as a function of the magnetic induction from 4.2°K to room temperature for two Ag-Pd alloys. The experimental results are shown in Fig. 1 for the 60% Pd sample and in Fig. 2 for the 80% Pd sample. The Hall coefficients, computed by means of Eq. (3) from the data shown in Figs. 1 and 2, are presented in Table I. The sign of the Hall coefficient is negative, corresponding to electronic conduction; and the magnitude is rather strongly temperature dependent. The Hall coefficient at 4.2°K is roughly $1\frac{1}{2}$ times larger than the Hall coefficient at room temperature. The values of R_0^* tabulated in Table I are plotted as a function of temperature in Fig. 3.

DISCUSSION

In the transition elements the *s* band overlaps a partially filled *d* band, and a two-band model must be used to make allowances for conduction in both bands. For a simple two-band model the Hall coefficient is given by

$$R_0=-(1/Nec)[(1/\nu_s)(\sigma_s/\sigma)^2-(1/\nu_d)(\sigma_d/\sigma)^2], \tag{5}$$

which depends on the mobility of the *s* electrons and the *d* holes only through the ratio $\beta=(\sigma_d/\sigma_s)$. This is readily demonstrated by writing the equation in the form

$$R_0=R_{0s}[1/(1+\beta)^2][1-(\nu_s/\nu_d)\beta^2], \tag{6}$$

where R_{0s} is that part of the Hall coefficient resulting from the *s*-band conduction. Although negative values of R_0 such that $|R_0|<|R_{0s}|$ might result from the presence of *d*-band conduction, negative values of R_0 such that $|R_0|>|R_{0s}|$ could not logically result from such a model. For 0.6 *s*-band electron per atom, which is required to explain magnetic susceptibility data, the expected values of R_{0s} are -15.5×10^{-13} volt cm/amp gauss for the 80% Pd alloy and -16.1×10^{-13} volt cm/amp gauss for the 60% Pd alloy. An examination

TABLE I. Experimentally determined values of R_0^* for 60% Pd−40% Ag and 80% Pd−20% Ag.

60% Pd−40% Ag		80% Pd−20% Ag	
Temperature (°K)	$10^{13}\times R_0^*$ (volt cm/amp gauss)	Temperature (°K)	$10^{13}\times R_0^*$ (volt cm/amp gauss)
4.2	−43.0	4.2	−35.2
20.0	−42.5	20.0	−33.5
77.0	−37.7	77.0	−28.7
169.0	−33.8	169.0	−23.2
231.0	−32.1	231.0	−21.9
302.0	−31.0	298.0	−20.1

[8] Emerson M. Pugh, Phys. Rev. **36**, 1509 (1930).

of Table I shows that $|R_0| > |R_{0s}|$, and hence the two-band model does not permit an interpretation of the Hall effect that is consistent with the accepted interpretation of the magnetic susceptibility data. This dilemma has been pointed out in connection with the Cu-Ni alloys[4] and more recently in connection with the Ag-Pd alloys.[9]

Although one can define an effective number of conduction electrons on the basis of a single band ($n^* = -1/R_0^* ec$), the value of n^* will vary with temperature since R_0^* is temperature dependent in both Cu-Ni and Ag-Pd alloys. In addition, it has been demonstrated that the Hall coefficient in those Cu-Ni alloys with a Curie point near room temperature must be corrected for a large $\partial M/\partial B$ contribution. Thus the concept of an "effective" number of charge carriers is unrealistic since the actual number of charge carriers should be independent of the temperature and the magnetic properties of the sample. Because the values of n^* at room temperature for the Ag-Pd alloys bear a close similarity to those obtained at the same temperature for the Cu-Ni alloys,[9] it has been suggested that the band model proposed by one of us does not fit the Cu-Ni results. In view of the unrealistic nature of n^*, we believe that such a superficial comparison of the two alloy series is unreliable and that R_0^* must be studied over a wide range of temperatures before an attempt is made to interpret the experimental values at any one temperature.

An examination of Fig. 3 indicates that the experimental values of R_0^* might obey an empirical relation of the form

$$R_0^* = A - C/(T-\theta). \tag{7}$$

Lavine[7] has found that the Hall coefficient for some Cu-Ni alloys follows such a relation for temperatures above their Curie point. Such a temperature variation in the Ag-Pd alloys suggests that the Hall coefficient consists of two parts. One part, which is the contribution in the high-temperature limit, is the one to be expected from the simple band model. On this basis, the temperature-dependent contribution, which increases with decreasing temperature, appears to be associated with the strong paramagnetism of these alloys. While the experimental results are not conclusive, they

TABLE II. The linear correlation coefficient, r, between $1/(R_0^* - A)$ and T for various values of A.

60% Pd–40% Ag		80% Pd–20% Ag	
$10^{13} \times A$ (volt cm/amp gauss)	r	$10^{13} \times A$ (volt cm/amp gauss)	r
−12.5	0.9905	−6.0	0.9964
−15.0	0.9922	−8.0	0.9974
−17.5	0.9941	−10.0	0.9980
−20.0	0.9961	−12.0	0.9970
−22.5	0.9980	−14.0	0.9956
−25.0	0.9986	−16.0	0.9862
−27.5	0.9921	−18.0	0.9653

[9] A. I. Schindler, Phys. Chem. Solids **1**, 42 (1956).

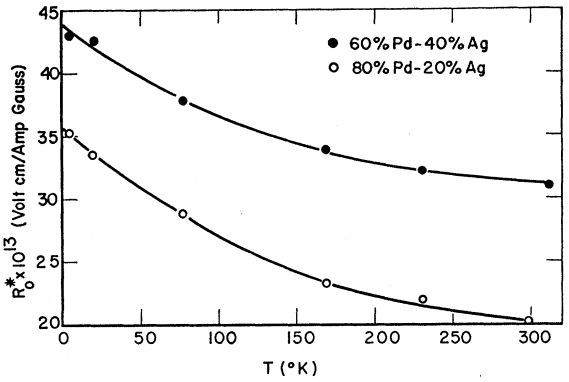

FIG. 3. Hall coefficient *versus* temperature for the two Pd–Ag alloys.

strongly suggest that the temperature variation is due to an extraordinary effect; i.e., from the $4\pi R_1 \chi$ term in Eq. (4). On this basis the A in Eq. (7) should be the true R_0 and θ should be a pseudo-Curie temperature. For ferromagnetic Cu-Ni alloys, the θ in Eq. (7) is the Curie temperature and is a well-defined positive quantity, but for these paramagnetic metals it is negative and is not defined.[10] We prefer to find that value of A for which the linear correlation coefficient, r, between $1/(R_0^* - A)$ and T is a maximum. The results obtained from such an analysis are presented in Table II. The fact that the linear correlation coefficient is nearly unity shows that Eq. (7) is a good representation of the data. Unfortunately, the correlation coefficients do not show a sharp maximum, and the empirical constants cannot be determined accurately by this method. It appears, however, that A is between -17.5×10^{-13} and -25.0×10^{-13} for the 60% Pd sample and between -8.0×10^{-13} and -14.0×10^{-13} for the 80% Pd sample. If d-band conduction can be neglected, these high temperature limits for R_0^* correspond to between 0.37 and 0.53 electron per atom for the 60% Pd sample and between 0.69 and 1.2 electron per atom for the 80% Pd sample. The rather large number of charge carriers in the 80% Pd sample may be due to the fact that d-band conduction is not entirely negligible in this alloy. These values seem to be in substantial agreement with the simple band model when the errors introduced by extrapolating to high temperatures are considered.

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[10] Hoare, Matthews, and Walling, Proc. Roy. Soc. (London) **A216**, 502 (1953).