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Kondo Effect in Amorphous Fe-Pd-Si and Co-Pd-Si Alloys*

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A Kondo-type resistivity minimum has been found in amorphous alloys obtained by rapid quenching from the liquid state and having the compositions $Fe_xPd_{80-x}Si_{20}$ and $Co_xPd_{80-x}Si_{20}$, in which x (in at.%) varies from 0 to 7 for Fe and from 0 to 11 for Co. Magnetic measurements indicate that these alloys become ferromagnetic at low temperatures. The resistivity and magnetoresistivity data are analyzed by the existing theories on the s-d exchange interaction. The results demonstrate that the coexistence of the resistivity minimum and ferromagnetism can be explained by the presence of small amounts of paramagnetic ions free from mutual interactions. This result is confirmed by magnetoresistivity measurements. The estimated values for the s-d exchange integral are -0.62 eV for the Fe-Pd-Si alloys and -0.42 eV for the Co-Pd-Si alloys.

I. INTRODUCTION

As shown by Kondo,[1] the dynamical nature of the localized spin system leads to the resistivity-minimum phenomenon in magnetically dilute alloys. This has been confirmed by a number of experimental results demonstrating that the Kondo logarithmic term in the resistivity is associated with the paramagnetic nature of the alloys. The existence of the noninteracting localized spin system has been assumed in later theoretical[2] and experimental[3] papers. Attempts to take into account the interacting localized spins in terms of an internal field have been made by several workers.[4-8] They found that the Kondo logarithmic term is suppressed by the internal field. Experimentally this has been evidenced by the decrease[7,8] of the absolute slope of the $\ln T$ term in the resistivity with increasing magnetic solute concentration and/or by the appearance of the resistivity maximum[9] below the resistivity minimum temperature. The latter phenomenon seems to be associated with the onset of magnetic ordering. Recent work[10] on both ferromagnetic and paramagnetic Ni-Cu alloys demonstrates that the Kondo effect disappears in the ferromagnetic alloys. These observations seem to indicate that the Kondo effect does not coexist with ferromagnetism in crystalline alloys which have been studied extensively so far.

In this paper, we discuss the results obtained for noncrystalline Pd-Si alloys containing Fe or Co and show that these results imply the coexistence of the Kondo effect with ferromagnetism in the amorphous alloys. The experimental technique for the present measurements is similar to that presented in previous papers.[11,12] The existence of a resistivity minimum in a ferromagnetic amorphous $Fe_{80}P_{13}C_7$ alloy has been reported already.[13] This, however, is not subject to a wide change in the magnetic-metal concentration. The present Pd-Si base amorphous alloys can contain from 0- to 7-at.% Fe or from 0- to 11-at.% Co, serving as one of the most suitable systems to study systematically the cases of dilute (paramagnetic) and concentrated (ferromagnetic) alloys.

II. RESULTS AND DISCUSSIONS

A. Amorphous $Fe_xPd_{80-x}Si_{20}$ Alloys

It has been established that the amorphous $Fe_xPd_{80-x}Si_{20}$ alloy ($0 < x \leq 7$) behaves like a paramagnet at high temperatures and like a ferromagnet at low temperatures.[14] The results of these measurements are summarized in Table I. Above

TABLE I. Results of the magnetic measurements for the $Fe_xPd_{80-x}Si_{20}$ alloys (taken from Ref. 14).

x	μ_{eff} (μ_B/atom) $T_d < T < 300$ °K	T_d (°K)	θ_p (°K)	T_c (°K)
0.5	5.73	1.7	1	···
1	5.78	45	11	···
3	5.85	50	30	···
5	5.60	95	64	···
7	5.60	160	110	28

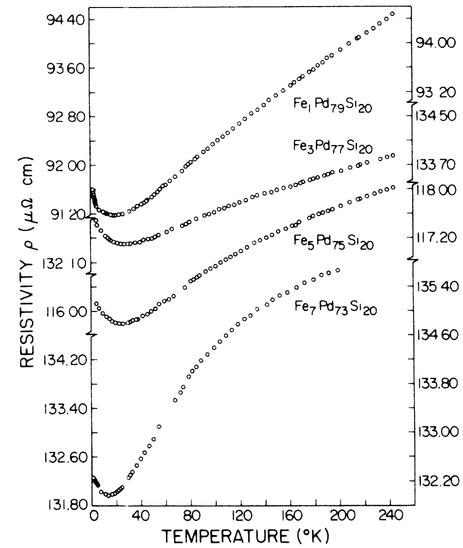

FIG. 1. Resistivity versus temperature for the $Fe_x Pd_{80-x}Si_{20}$ alloys.

the temperature T_d,[15] the susceptibility of the amorphous alloys obeys the Curie-Weiss law, through which the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_p were determined. The ferromagnetic Curie temperature T_c has been obtained by plotting H/σ_a versus σ_a^2, where H is the magnetic field and σ_a is the magnetization per Fe atom.[16] Between T_d and T_c, the amorphous alloys are superparamagnetic.

The resistivity measured for the amorphous $Fe_xPd_{80-x}Si_{20}$ alloys is plotted in Fig. 1 as a function of temperature. It is noticed that the resistivity minimum effect becomes smaller when the Fe concentration is high, which is different from the case of the amorphous alloys containing Cr or

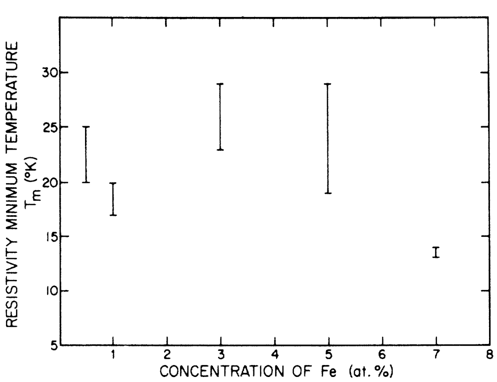

FIG. 2. Resistivity minimum temperature vs Fe concentration for the $Fe_xPd_{80-x}Si_{20}$ alloys (taken from Ref. 11).

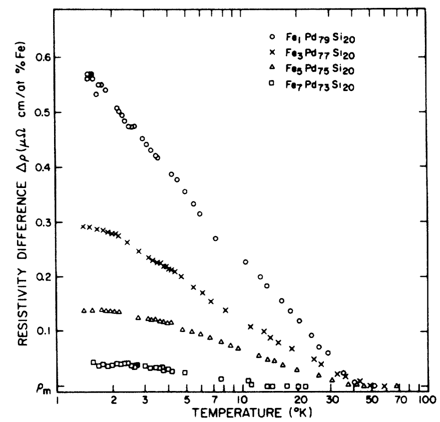

FIG. 3. Resistivity difference per at.% Fe vs temperature for the $Fe_xPd_{80-x}Si_{20}$ alloys. The values of ρ_m are 19.25, 11.95, 4.11, and 4.62$\mu\Omega$ cm for $x=1$, 3, 5, and 7, respectively.

Mn.[12] The resistivity minimum temperature T_m also decreases with increasing Fe concentration for $x>3$, which is shown in Fig. 2. These observations are linked with the unusual results that the resistivity minimum phenomenon can coexist with ferromagnetism. This is seen in a comparison of Fig. 2 and Table I, showing that $T_m < T_c$ for $x=7$. This result seems to contradict the Kondo prediction. However, the present observation may be due to the presence of paramagnetic ions in the ferromagnetically ordered alloys. Such a peculiar phenomenon has been observed in the amorphous alloys containing Co,[17] and may be associated with the fact that d-d spin interaction is about 50% weaker in the amorphous alloys than in the corresponding crystalline alloys.[14] The decrease of T_m with increasing Fe concentration above 3 at.% suggests that the number of the "free" localized spins tends to decrease with increasing Fe concentration. A change of slope in the resistivity-temperature curve was observed around θ_p for the concentrated Fe alloys. Such an anomaly has been attributed to the scattering of the conduction electrons into the nonconducting d states.[18]

To interpret the resistivity data, we write the total resistivity at low temperatures in the form[12]

$$\rho = \alpha + \delta T^2 + \gamma \ln T \,, \qquad (1)$$

TABLE II. Values of γ and the resistivity minimum temperature calculated by using the value of γ in Eq. (2) for the $Fe_xPd_{80-x}Si_{20}$ alloys.

x	$\gamma(\mu\Omega$ cm)	T_m(°K)
0.5	−0.223	20.0
1	−0.174	17.7
3	−0.260	21.6
5	−0.286	22.6
7	−0.163	17.1

TABLE III. Values of p and q in the expression $\Delta\rho_H/\rho_{H=0} = -pH - qH^2$ for the amorphous $Fe_xPd_{80-x}Si_{20}$ alloys.

x	$p(10^{-4}/\text{kOe})$	$q[10^{-5}/(\text{kOe})^2]$
0.5	0.136	0.075
1	0.115	0.410
3	0.940	1.09
5	1.84	1.82
7	9.15	0

where the first term represents the temperature-independent residual resistivity, the second term the temperature-dependent nonmagnetic part of the resistivity, and the third the Kondo-logarithmic term. The magnetic part of the resistivity ($\Delta\rho$) consisting of a part of α and of the third term in Eq. (1) is obtained by subtracting the resistivity of the amorphous $Pd_{80}Si_{20}$ alloy from the total resistivity of a $Fe_xPd_{80-x}Si_{20}$ alloy. The resistivity difference $\Delta\rho$ per Fe concentration is plotted against temperature in Fig. 3, from which the value of γ is obtained and is listed in Table II. Equation (1) gives a resistivity minimum temperature at

$$T_m = (-\gamma/2\delta)^{1/2} . \qquad (2)$$

The values of T_m calculated by taking $\delta = 2.8\times10^4$ $\mu\,\Omega\,\text{cm}$ [12](for the $Pd_{80}Si_{20}$ alloy) are given in Table II. These values of T_m agree quite well with the observed ones plotted in Fig. 2. This indicates that Eq. (1) can be used to describe the temperature dependence of the resistivity between T_m and the temperature T_d' where $\Delta\rho$ starts to level off. In other words, for $T_d' < T < T_m$ we can neglect the resistivity term which was considered by Silverstein[6] to take into account the interaction between localized spins. It is noticed that the concentration dependence of T_m is different from that for the crystalline alloys where T_m is proportional to the $\frac{1}{5}$ power of concentration. This difference arises from the fact that the temperature-dependent resistivity term for the amorphous $Pd_{80}Si_{20}$ varies as T^2 instead of T^5 and that γ is not proportional to Fe concentration in the present alloys. It is also noticed in Fig. 3 that T_d' increases as the Fe concentration increases. This feature is similar to the case for a Cu alloy containing small amounts of Cr for which the temperature where the resistivity becomes temperature-independent increases with an increasing magnetic field.[19] These results may arise from the same origin since the flattening out of $\Delta\rho$ occurs in the region where the internal field is probably large.

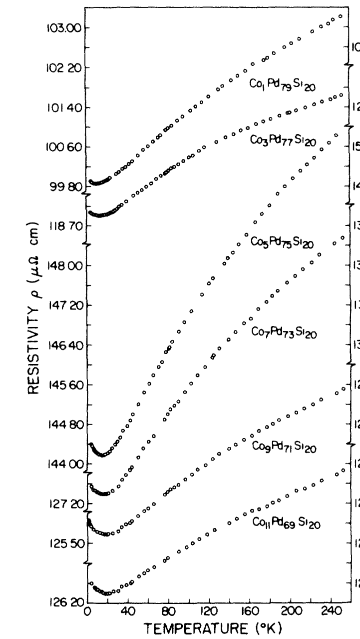

FIG. 5. Resistivity vs temperature for the $Co_xPd_{80-x}Si_{20}$ alloys.

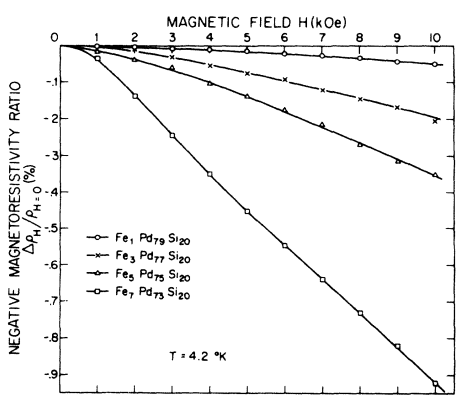

FIG. 4. Negative magnetoresistivity ratio vs magnetic field at 4.2 °K for the $Fe_xPd_{80-x}Si_{20}$ alloys.

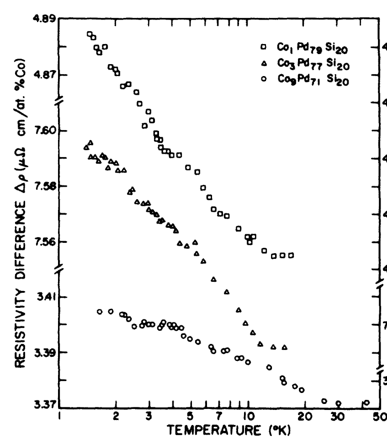

FIG. 6. Resistivity difference per at.% Co vs temperature for the $Co_xPd_{80-x}Si_{20}$ alloys.

TABLE IV. Values of γ and the resistivity minimum temperature calculated by using the value of γ in Eq. (2) for the $Co_xPd_{80-x}Si_{20}$ alloys.

x	γ($\mu\Omega$cm)	T_m(°K)
1	−0.04	8.5
3	−0.143	16.0
5	−0.197	18.7
7	−0.137	15.8
9	−0.142	15.9
11	−0.181	18.0

By using Eq. (8) of Ref. 12 with $\gamma = -0.223$ $\mu\Omega$cm (for the $Fe_{0.5}Pd_{79.5}Si_{20}$ alloy), $S=\frac{3}{2}$,[14] and $E_F = 3.5$ eV,[12] we obtain the value of the s-d exchange integral $J_{sd} \sim -0.62$ eV. This value is larger than those ($J_{sd} = -0.1$[20] to -0.25 eV[1]) obtained for crystalline Au alloys containing small amounts of Fe for which $S=\frac{4}{2}$,[21] but compares favorably with those ($J_{sd} = -0.6$[19] to -1.2 eV[22]) found in crystalline Cu alloys containing small amounts of Fe for which $S=\frac{3}{2}$. These results again indicate that the value of J_{sd} is the largest when S is close to $\frac{2\pm 5}{2}$ as pointed out in our previous paper.[12]

The magnetoresistivity of the amorphous Fe-Pd-Si alloys was measured at 4.2, 77, and 295 °K, and corrected by subtracting the value obtained for the amorphous $Pd_{80}Si_{20}$ alloy. The corrected magnetoresistivity

$$\rho_H = \rho_H(Fe_xPd_{80-x}Si_{20}) - \rho_H(Pd_{80}Si_{20})$$

is negative with respect to the zero-field value

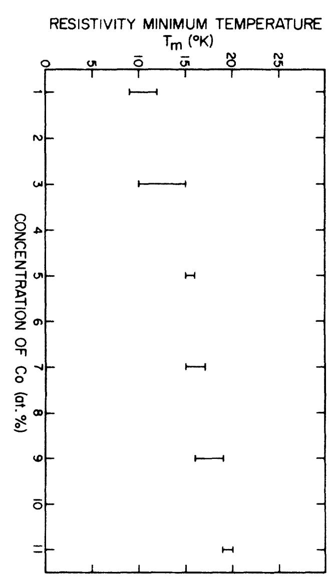

FIG. 7. Resistivity minimum temperature vs Co concentration for the $Co_xPd_{80-x}Si_{20}$ alloys (taken from Ref. 11).

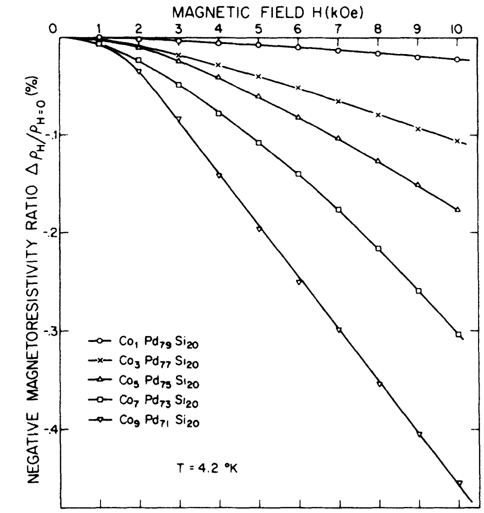

FIG. 8. Negative magnetoresistivity ratio vs magnetic field at 4.2 °K for the $Co_xPd_{80-x}Si_{20}$ alloys.

$\rho_{H=0}$. The magnetic field dependence of the value

$$\Delta\rho_H/\rho_{H=0} = (\rho_H - \rho_{H=0})/\rho_{H=0}$$

is shown in Fig. 4. For $H > 4$ kOe, these data can be expressed by

$$\Delta\rho_H/\rho_{H=0} = -pH - qH^2 \quad (p, q > 0;\ H \text{ in kOe})$$

with p and q listed in Table III. Yosida[23] has shown that for a ferromagnet the magnetoresistivity is proportional to $-H$ and for a paramagnet it is proportional to $-H^2$, and this behavior is attributed to an s-d exchange interaction. In the present case, however, the magnetoresistivity proportional to $-H$ is probably due to the superparamagnetic clusters[14] behaving like a ferromagnet at higher fields. It was found that the $Fe_7Pd_{73}Si_{20}$ alloy becomes ferromagnetic below T_c (= 28°K).[14] The magnetoresistivity $\Delta\rho_H/\rho_{H=0}$ of this alloy at 4.2°K varies as $-H$ for $H > 3$ kOe as expected, and varies as $(-2.0H - 2.7H^2)\times 10^{-4}$ for $0 < H \leq 3$ kOe. This result suggests that ferromagnetism and paramagnetism coexist in the amorphous alloy con-

TABLE V. The values of q and n in the expression of $\Delta\rho_H/\rho_{H=0} = -qH^n$ for the amorphous $Co_xPd_{80-x}Si_{20}$ alloys.

x	T=4.2 °K		T=77 °K	
	$q(10^{-6})$	n	$q(10^{-6})$	n
1	7.6	1.48	...	...
3	31.6	1.49	1.7	1.35
5	46.3	1.58	4.9	1.42
7	105	1.47	17.9	1.41
9	261	1.24 ($H > 4$ kOe)	39.7	1.63

taining 7-at.% Fe even for $T < T_c$, and this is consistent with the resistivity minimum found in this alloy below T_c. Even though the paramagnetic part of the magnetoresistivity can be extracted from the observed magnetoresistivity, quantitative agreement with the theoretical results of Béal-Monod and Weiner[24] is rather poor. A qualitative agreement with the theory, however, can be attained if the measured magnetizations are considered. As seen in Ref. 14, the magnetization σ_a(8.4 kOe) is approximately constant for $0.5 < x < 5$ and is proportional to x for $x \geqslant 5$. The absolute value of the negative magnetoresistivity at $H = 8.4$ kOe increases somewhat linearly with Fe concentration x for $x < 5$ and more rapidly with x for $x > 5$. This is consistent with the concentration dependence of the magnetization σ_a in the light of the relation[24] $\Delta\rho_H \propto -x\sigma_a^2$.

B. Amorphous $Co_xPd_{80-x}Si_{20}$ Alloys

It has been shown that the magnetic properties of the amorphous Co-Pd-Si alloys can be explained by postulating the existence of superparamagnetic clusters.[17] Even for the alloys containing more than 9-at.% Co which have significant magnetic moments at room temperature, paramagnetic regions are found to coexist with ferromagnetic regions at lower temperatures. These results seem to be consistent with the low-temperature resistivity data which show a Kondo-type resistivity minimum (Fig. 5). As in the case of the amorphous Fe-Pd-Si alloys, the resistivity data of Fig. 5 can be expressed by Eq. (1), and the resistivity minimum temperature T_m is given by Eq. (2). If the resistivity contribution ($\Delta\rho$) from Co atoms is again assumed to be the difference between the resistivity of a Co-Pd-Si alloy and that of the $Pd_{80}Si_{20}$ alloy (Fig. 6), the values of γ and of T_m are obtained and given in Table IV. A good agreement between the values of T_m and the observed ones shown in Fig. 7 suggests that the internal field dependent term proposed by Silverstein[6] can be neglected above the temperature T_d' where the leveling off of $\Delta\rho$ takes place. The fact that T_d' increases with increasing Co concentration suggests that the leveling off of $\Delta\rho$ below T_d' has the same origin as that observed in the amorphous Fe-Pd-Si alloys. By using Eq. (8) of Ref. 12 with $\gamma = -0.43$ $\mu\Omega$cm/at.%Co (for $x \leqslant 5$), $S = \frac{1.7}{2}$,[17] and $E_F = 3.5$ eV, the value of J_{sd} is found to be -0.42 eV.

The magnetoresistivity data obtained at 4.2, 77, and 295°K were corrected as in the case of the amorphous Fe-Pd-Si alloys. The results at $T = 4.2$°K are shown in Fig. 8. The corrected magnetoresistivity at 4.2 and 77°K can be expressed by a relation $\Delta\rho_H/\rho_{H=0} = -qH^n$, where q and n are listed in Table V. The value of $\Delta\rho_H$ varies approximately as $-H^{3/2}$ except for the case of $x = 9$. This result may be associated with the existence of superparamagnetic clusters.[25] This is open to speculation however, since there is no theory of magnetoresistivity for superparamagnetically ordered alloys. The fact that n approaches one when x is large ($x > 7$) suggests the dominance of the ferromagnetically ordered regions in these alloys. As in the case of the amorphous Fe-Pd-Si alloys, the value of $\Delta\rho_H/\rho_{H=0}$ varies as $-x\sigma_a^2$ if σ_a is the measured magnetization. This is reflected in the relation between $\Delta\rho_H/\rho_{H=0}$ and Co concentration x. It is found from Fig. 8 that $\Delta\rho_{H=8.4\text{ kOe}}/\rho_{H=0}$ is proportional to $-x^{1.6}$. On the other hand, according to Ref. 17, σ_a(8.4 kOe) is proportional to $x^{0.3}$, which gives

$$\Delta\rho_{H=8.4\text{ kOe}}/\rho_{H=0} \propto -x\sigma_a^2 = x^{1.6}.$$

III. CONCLUSIONS

The resistivity minimum observed in the amorphous Fe-Pd-Si and Co-Pd-Si alloys is of the Kondo type. The unusual coexistence of the Kondo effect and the apparent ferromagnetic ordering can be explained by the existence of a small amount of paramagnetic ions in the alloys. These paramagnetic ions seem to be relatively "free" from each other since the resistivity data (between T_m and T_d') could be explained without taking into account the term arising from the mutual interaction between the paramagnetic ions. This is probably linked with a small d-d interaction in the amorphous alloys. The leveling off of the resistivity at lower temperatures, however, is probably due to the internal field arising from the ferromagnetic ordering of the free ions. From the coefficients of the logarithmic term of the resistivity for the alloys containing a small amount of Fe or Co, the values of the s-d exchange integral (J_{sd}) are determined. The results give $J_{sd} \sim -0.62$ eV for the Fe-Pd-Si alloys and $J_{sd} \sim -0.42$ eV for the Co-Pd-Si alloys. When the alloys have an appreciable amount of paramagnetic ions coexisting with superparamagnetic clusters (e.g., Fe-Pd-Si alloys), the magnetoresistivity at higher fields varies as $-pH - qH^2 (p, q > 0)$ as expected. In the case of Co-Pd-Si alloys where the alloys are predominantly superparamagnetic, the magnetoresistivity varies as $-H^{3/2}$. In both cases, however, the magnetoresistivity varies approximately as $-\sigma_a^2$ where σ_a is the measured magnetization, and this is consistent with the theoretical result of Béal-Monod and Weiner.

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