Ferromagnetic and spin-glass ordering in Fe-doped Au_xPd_{1-x} alloys

E. R. Domb* and D. J. Sellmyer Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588

T. M. Quick and R. J. Borg

Lawrence Livermore Laboratory, University of California, Livermore, California 94550 (Received 17 October 1977)

Ferromagnetic and spin-glass ordering has been studied in $(Au_{x}Pd_{1-x})_{1-c}Fe_{c}$ alloys for $0 \le x \le 1$ and $0 \le c \le 0.06$. Magnetic susceptibility, high-field magnetization, and Mössbauer measurements have been performed between liquid-helium and room temperature. For small x_i the alloys are strongly exchange enhanced. Assuming that the local-moment-conduction-electron exchange coupling J is independent of x, and employing the Takahashi-Shimizu-Doniach-Wohlfarth theory, we obtain J = 0.12 eV from the saturation moment versus host susceptibility data. The theory, however, fails to describe the interimpurity coupling that leads to magnetic order in the Pd-rich alloys. A simple phenomenological model, based on the ferromagnetic coupling of all the giant polarization clouds except those that are "isolated," gives qualitative agreement with the $T_c(c)$ data, where T_c is the ordering temperature. The magnetic ordering changes from ferromagnetic to spin glass or mictomagnetic as x increases beyond about 0.5. This seems to be connected with the change at this composition in the character of the electronic states at the Fermi level from d-like to s-like. The Au-rich samples are spin glasses understandable in terms of the Sherrington-Southern theory which is based on fluctuations in the exchange couplings of the Fe spins. The magnitude of this coupling was estimated in two ways, employing the theories of Sherrington-Southern and Larkin, and the results were in reasonable agreement with each other.

I. INTRODUCTION

The development of an ordered magnetic state in a disordered alloy is an interesting problem in the broader field of the physics of disordered materials. One can distinguish at least two classes of magnetic order in alloys: ferromagnetic and spin-glass or mictomagnetic. In ferromagnetic alloys it is assumed that all the moment-bearing atoms have their spins aligned below the Curie temperature even though the positions of these atoms are essentially random. In the spin glasses one is dealing normally with a small concentration, for example, several percent, of magnetic atoms in a nonmagnetic host metal. The prototypical spin-glass alloys are Cu(Mn) and Au(Fe), though many other examples are known.¹ The moments in a spin-glass alloy are coupled via an oscillatory interaction involving the conduction electrons. Below a certain temperature T_{sg} , the spins "freeze" in their quasirandom orientations, though there may be magnetic order on a short-range basis. The sample as a whole has no net moment in zero applied field. On the other hand, dilute alloys such as Pd(Fe) develop ferromagnetic order at low temperatures and dilute Pd(Mn) alloys have a complex phase diagram in which the ferromagnetic or spin-glass ordering depends on the Mn concentration.²

The binary alloy systems Au(Fe) and Pd(Fe)behave quite differently. For example, for dilute Au(Fe) alloys the spin state is normal,³ the magnetic ordering is spin glass in nature,⁴ the hyperfine field is rather small, there is a large nuclear quadrupole splitting, the isomer shift is large,⁵ and the coercive field is relatively large.⁴ On the other hand for dilute Pd(Fe) alloys, there is a giant magnetic moment, the ordering is ferromagnetic, the hyperfine field is large, there is essentially no nuclear quadrupole splitting, the isomer shift is small, and the coercive field is small.²

An important aspect of the nature of dilute magnetic alloys is the extent to which s or d character of the host electronic structure controls the nature of the magnetic order. The object of the present work was to study this question in dilute Fe-doped Au Pd₁₋, alloys. Two issues are involved; one is the sign of the local-moment-conduction-electron coupling, and the other is the nature of the longer-range interimpurity coupling. For the former problem, there is antiferromagnetic coupling in Au(Fe) leading to the Kondo effect, but ferromagnetic coupling leading to giant moments in Pd(Fe). For the latter problem, the Ruderman-Kittel interaction in Au(Fe) is believed to be the mechanism for spin-glass ordering, whereas the ferromagnetic coupling between the giant polarization clouds in Pd(Fe) does not have a satisfactory theoreti-

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cal description. In our ternary-alloy system, there is the opportunity in principle to study these questions as the host-electronic structure is varied. Furthermore, dilute systems of this type may be simpler to understand than *concentrated* disordered magnetic alloys.

Until a few years ago, models for the host-band structure of alloys like Au-Pd or Ag-Pd were based on the old idea of noble-metal s electrons filling the dbands of Pd near the equiatomic composition. However, recent electronic-structure calculations for Ag-Pd,⁶ based on the coherent-potential approximation, give rather good agreement with photoemission and electronic-heat-capacity data. The theoretical and experimental results show that the rigid-band and virtual-crystal models are untenable, and the theory points the way towards a model which can account for localized effects such as charge-transfer and localizedpotential functions. Therefore, in dilute magnetic alloys based on hosts such as these, the conditions for moment formation and the spin-fluctuation temperatures may well depend on the local environment of the magnetic impurity in question.

There are additional reasons for interest in dilute magnetic alloys based on hosts such as Au-Pd or Ag-Pd. In both of these hosts, with no Fe doping, there is evidence for spin-fluctuation effects (resistance minima, etc.) at the critical concentration for "*d*-band filling" (on the old rigid-band model).⁷ Secondly, there is an opportunity in systems of this type, to "turn off" the exchange enhancement of Pd in a controlled way by adding Au. Thus, we are able to compare the results for Pd-rich alloys with the theories of Takahashi and Shimizu,⁸ and Doniach and Wohlfarth,⁹ who discussed ferromagnetic ordering in exchange-enhanced alloys.

Some work on Fe-doped alloys such as Ag-Pd and Au-Pd has already appeared. Longworth measured Mössbauer spectra in the Au-Pd(Fe) system and found a marked change in the isomer shift, linewidth, and hyperfine field at about 50-at. % gold.¹⁰ Qualitatively, his results were confirmed by the present study. Quick et al.¹¹ reported some anomalous line displacements and widths in the Mössbauer spectrum and interpreted these as spin-relaxation effects which are associated with the ferromagnetic-nonferromagnetic transition at about 50-at. % gold. In the present work we have combined bulk susceptibility and high-field magnetization measurements with Mössbauer measurements in order to obtain further information on the magnetic ordering. Similar measurements have been carried out in the Ag-Pd(Fe) system by Budnick, Levy, and co-workers,¹²⁻²⁴ by Brill and Wortman,^{15, 16} and by De Benedetti et al. 17

II. EXPERIMENTAL

Throughout this paper the samples will be denoted by the formula $(Au_xPd_{1-x})_{1-c}Fe_c$. The alloys were made by melting either in an argon-arc furnace or in an electron-beam furnace. Following repeated melting, the Mössbauer samples were alternatively vacuum annealed and cold rolled to form foils. Finally, both the Mössbauer and susceptibility samples were annealed for 2 h in quartz ampules which were then broken in ice water for rapid quenching. The materials used were 99.9999% pure Au, 99.995% pure Pd, and Fe metal isotopically enriched to 91% in ⁵⁷Fe. The compositions were determined by chemical analysis to a precision of 0.01 at.%. The lattice parameters were determined by x-ray diffraction. The source purchased from New England Nuclear Corp. consisted of ⁵⁷Co deposited on and diffused into a 0.001-in. copper foil.

The Mössbauer spectrometer is of the constant acceleration sort. The detector is a NaI scintillation counter and data is stored in a Scipp multichannel analyzer. The cryogenic system and the other Mössbauer apparatus have been described in detail elsewhere.¹⁸

Magnetic susceptibility was measured as a function of temperature from 1.5 to 300 K using a Faraday susceptibility apparatus that has been described previously.¹⁹ Measuring fields ranged from 1 to 10.4 kOe. The high-temperature data were analyzed using a least-squares fit to the Curie-Weiss law

$$\chi(T) = \chi_0 + (C/T - \Theta) \quad , \tag{1}$$

$$C = N_{\mu}\mu_{e}^{2}/3k_{B} \quad , \tag{2}$$

$$\mu_e = g \,\mu_B [S(S+1)]^{1/2} \quad , \tag{3}$$

where Θ is the Weiss temperature, N_i is the number of iron atoms, μ_e the effective moment, and S the apparent spin value.

μ

Magnetic moment σ was measured as a function of temperature T and field H, from 1.5 to 40 K and from 0 to 80 kOe in a vibrating sample magnetometer (VSM) in a Janis Varitemp Dewar. The demagnetizing factor for the samples was determined using the slope of the σ -vs-*H* curve for the x = 0.094, c = 0.038sample in the low-temperature region where its behavior was clearly ferromagnetic. All the samples were cylinders approximately 2 mm in diameter and 3 mm long. Temperature was controlled above 4.2 K by a capacitance thermometer, the output of which regulated the amount of heat put into the He gas. The temperature near the sample was measured using a calibrated Si diode, and typically varied by less than 0.1 K during a sweep from zero field to 80 kOe to zero field.

III. RESULTS

A. Mössbauer

Table I lists the analyzed compositions, ordering temperatures, and saturation hyperfine fields for the

TABLE I. Analyzed compositions, ordering temperatures, and saturation hyperfine fields of Mössbauer samples. The sample composition is denoted by $(Au_xPd_{1-x})_{1-c}Fe_c$

x	C	T_0 (K)	H _{sat} (kOe)
1.000	0.026	18	241
0.778	0.030	15	248
0.728	0.025	15	256
0.669	0.025	15	262
0.500	0.026	12	281
0.348	0.031	15	286
0.229	0.027	20	295
0.055	0.034	74	310
0.000	0.025	93	311

Mössbauer-effect samples. As previously mentioned, these results, in the main, support those which were earlier reported by Longworth¹⁰ although frequently differing in detail and actual magnitude. The most striking feature revealed by both studies is the discontinuity in the behavior of several Mössbauer parameters near the equiatomic composition at which the al-



FIG. 1. Magnetic-ordering temperature T_0 and the saturation nuclear magnetic hyperfine field as a function of composition. There is a vague minimum in T_0 about AuFe but no correspondingly significant variation in H_{sat} in the same region.

loys transform from spin-glass to ferromagnetic order.

The temperature dependence of the hyperfine splitting for all compositions is well fit by a Brillouin function with spin values ranging from J = 1 to J = 3. The transition from the disordered to the ordered state is quite sharp and there is no evidence of a tail in the region just above T_0 as reported by Longworth; i.e., for $T > T_0$ the reduced magnetization H_n is zero for all alloys investigated. We have established in a separate investigation²⁰ that failure of H_n to vanish for $T > T_6$ results from a nonrandom distribution of solute and is not the case if specimens are truly homogeneous.

Figure 1 shows the variation in magnetic ordering temperature and saturation hyperfine field as a function of composition. Although far from pronounced there is an indistinct minimum in T_0 in the vicinity of the equiatomic composition. The plot of H_{sat} versus composition also undergoes no distinctive fluctuations at the same composition. In contrast, the isomer shift both below and above T_0 shows a definite shift between 40- and 50-at. % Pd as shown in Fig. 2 although it is rather less pronounced for the ordered state.

Figure 3 shows both spectra and room temperature quadrupole splittings for all compositions. The spectra are fitted by combining a singlet and doublet for $Au_{0.98}Fe_{0.02}$, with an unconstrained doublet for speci-



FIG. 2. Isomer shift for $T < T_0$ and $T > T_0$, i.e., 4.6 °K and ~ 298 °K. Note the apparent large discontinuity in the vicinity of (40-50)-at. % Pd.



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FIG. 3. Calculated quadrupole splittings (right panel) for the room-temperature spectra (left panel). Note the change in appearance of the spectra at the equiatomic concentration.

mens with $0.669 \le x \le 0.778$ and with a doublet of equal linewidths for specimens with $0 \le x \le 0.5$. There is an intuitive physical basis for such varied fitting procedures²¹ but it is perhaps more meaningful to merely note the change in character of the actual spectra at the 50-50 composition. Below T_0 the quadrupole splitting is zero for all compositions.

Figure 4 shows the apparent variation in the nuclear-moment ratio of the excited to ground state as



FIG. 4. Apparent variation in the ratio of the nuclear moments of the excited and ground states caused by spin relaxation induced by the magnetic transformation in the vicinity of x = 0.5.

a function of composition. The ratio of the excited to ground-state moment increases significantly at the midpoint of the composition range. The true value of this ratio is a nuclear property unaffected by local chemical environment and the departure from constancy reflects a difference in nuclear spin-flip relaxation, presumably induced by the transformation from random antiferromagnetic to ferromagnetic about the 50-50 composition; this observation has been reported elsewhere.¹¹ It is interesting to note that this fluctuation does not occur with the abruptness demonstrated by the quadrupole splitting. This observation suggests that the transition from spin-glass to ferromagnetic order is but weakly dependent upon composition. To the best of our knowledge there are no similar transitions in other materials with which to compare this observation.

We did not perform polarization measurements as did Longworth.¹⁰ His results clearly demonstrate the transition from spin-glass to ferromagnetic occuring at about 55-at. % Au.

B. Magnetization and magnetic susceptibility

Table II lists the analyzed compositions, ordering temperatures, effective moments, and spin values for the specimens studied by the Faraday measurements. The Faraday susceptibility data for all samples obeyed the Curie-Weiss relation [Eq. (1)] at high temperature. At low temperature, the data for the nominally 2-at. % Fe samples having x = 1.00 and 0.762 had maxima in χ as a function of temperature; those for the other materials had irregularities in slope at low temperatures, indicating the onset of some kind of magnetic order, as seen in Fig. 5. Figure 6 shows the Faraday data for several of the 6-at. % Fe samples. μ_c values for the 6-at. % Fe samples are not listed in Table II because the paramagnetic data cannot be well

TABLE II. Analyzed compositions, ordering temperatures, effective moments, spin values, and saturation moments per Fe atom for the magnetization samples.

x	С	<i>T</i> ₀ (K)	$\mu_e \ (\mu_B)$	S	$\mu_s(\mu_B)$	
1.000	0.021	11.7ª	3.4	1.3	ND	
0.762	0.022	9.6 ^a	5.4	2.3	ND	
0.503	0.021	8.0	6.4	2.7	4.5	
0.245	0.022	10.0	8.2	3.6	5.3	
0.094	0.038	31.0	10.2	4.6	6.1	
0.773	0.061	19 ± 3 ^a	ND ^b	ND	ND	
0.501	0.060	78 ± 6	ND	ND	ND	
0.236	0.060	96 ± 6	ND	ND	ND	

^aDetermined from maximum in M/H vs T as shown in Fig. 6. ^bND: not determined.



FIG. 5. Temperature dependence of the susceptibility of the Au_xPd_{1-x} samples with nominal Fe concentrations ranging from 2 to 4 at.%. Note the weak maxima in the x = 1 and x = 0.75 samples as compared with the large low-temperature susceptibilities of the x = 0.09, 0.25, and 0.50 samples.

fitted with a Curie-Weiss law. Presumably, because of the relatively high Fe concentration, there are Fe-Fe interactions which lead to the above behavior. This phenomenon is discussed by Window.²² Because of the high fields used to measure χ , the behavior of χ for $T < T_c$ cannot be interpreted in a simple manner.

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The ordering temperature T_c was determined for ferromagnetic materials using the method described by McGuire and Flanders²³ of extrapolating the maximum of $d\chi/dT$ to H = 0. The effective moment was found, as described above, by a least-squares fit to the Curie-Weiss law. The spin was found assuming that g = 2 and that all Fe atoms have the same spin.

High-field magnetization measurements at 4.2 K for the 2-at.% Fe samples are shown in Fig. 7. For x = 0.502, the moment was not saturated at 80 kOe, so the assumption $\mu(H) = \mu_s(1 - a/H)$ was used to find μ_s by extrapolation.²⁴ Table II lists the saturation moments per impurity for the ferromagnetic samples.

Hysteresis loops for the ferromagnets were very narrow. In contrast, the x = 1 and x = 0.762 samples had broader hysteresis loops, with coercive fields of 2.1 and 1.1 kOe at 1.4 K, respectively, as seen in Fig. 8. There was no detectable displacement (less than 30 Oe) of the hysteresis loops when the materials were cooled from 35 to 1.4 K in an 80-kOe field. Borg and Kitchens⁴ have shown that the shift is very slight in Au(Fe) alloys, in contrast to the displacement of the loops in Cu(Mn) and Au(Mn). They saw a displace-



FIG. 6. Temperature dependence of the apparent susceptibility σ/H for the nominal 6-at. %-Fe samples. For x = 0.24 and 0.50, the behavior is characteristic of a ferromagnet, whereas for x = 0.77, mictomagnetic/behavior is suggested.



FIG. 7. High-field magnetization of the more dilute Fe samples. A: -x = 1.0, c = 0.021; B: -x = 0.762; c = 0.022; C: -x = 0.503, c = 0.021; D: -x = 0.245, c = 0.022; E: -x = 0.094, c = 0.038.

ment of approximately 200 Oe in Au₉₅Fe₅ cooled in a 12.5-kOe field. Vibrating-sample-magnetometer measurements of the initial slope of the M vs H curves, see Fig. 9, show cusps that are characteristic of spinglass materials. To make these measurements, the samples were heated to above 35 K (remanence vanished near 20 K) then cooled to the temperature of interest. Initial slope versus temperature is also shown for the x = 0.502, c = 0.021 sample. The curve is not cusplike, but rather looks like the susceptibility of a ferromagnet.

The remanence of Au_{0.98}Fe_{0.02} shows a pronounced time dependence, as has been seen for other spin glasses.⁴ As in these other cases, the remanence decays, but does not fit an expression of the form $\sigma(t) = \sigma_0 + ae^{-\lambda t}$. Materials containing Pd showed no time dependence of the remanence.



FIG. 8. Partial hysteresis loops at 1.4 K for the spin glass or mictomagnetic samples; $c \simeq 0.02$. The complete loops have inversion symmetry about the origin.



FIG. 9. Low-field susceptibility data taken from VSM data of M(H) in the limit $H \rightarrow 0$. Note the peaks characteristic of spin glasses for the bottom two curves, and the apparent ferromagnetic behavior of the top curve.

IV. DISCUSSION

A. Exchange-enhanced ferromagnetic alloys

It is natural to determine at the outset whether the data for our Au-Pd(Fe) alloys can be understood in terms of existing molecular-field theories for exchange-enhanced alloys. Let us briefly outline the results of these theories. Takahashi and Shimizu⁸ developed a theory for Pd-based alloys containing localized moments which assumes: a molecular-field interaction, of strength α , between the bare-localized moments and the 4d band electrons; that the rigidband model is valid for the 4d band; that direct interactions between the magnetic impurities can be ignored; that α is independent of the impurity concentration; and that the polarization of the 4d band is spatially uniform. Doniach and Wohlfarth⁹ found the same results using a linear-response approximation, without the assumptions of a rigid-band model or a uniform-band polarization. Kim²⁵ found similar results though his viewpoint emphasizes ferromagnetism of the itinerant electrons rather than the ordering of localized moments, as in the other approaches. Nieuwenhuys² has given a critique of these theories as applied to dilute Pd alloys containing Fe, Mn, and Co.

The major predictions of the Takahashi-Shimizu and Doniach-Wohlfarth (hereafter denoted TSDW) theories are

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$$T_{c} = N_{c}g^{2}\mu_{B}^{2}s(s+1)\alpha^{2}\chi_{0}(T_{c})/3k_{B} , \qquad (4)$$

$$\mu_e = g \,\mu_B[s\,(s+1)]^{1/2}[1 + \alpha \chi_0(T)] \quad , \tag{5}$$

$$\mu_{\lambda} = g \mu_{B} s \left[1 + \alpha \chi_{0}(T_{c}) \right] \quad , \tag{6}$$

$$J = \frac{1}{2} N g^2 \mu_B^2 \alpha \quad , \tag{7}$$

where $x_0(T)$ is the host alloy susceptibility, $x_0(T_c)$ is the host susceptibility at the ordering temperature of the Fe-doped alloy, s is the bare spin on the magnetic impurity to which we assign a value of $\frac{3}{2}$, g is the g factor taken as 2, J is the exchange interaction between the local moment and the 4d conduction electrons, and N is the total number of atoms.

Previous work on Ag-Pd(Fe) has generally confirmed the TSDW theories. In particular, Levy et al.¹² tested Eq. (4) and found that there was a linear increase in T_c with $\chi_0(T_c)$ – although the straight line derived from the data did not go through the origin of the T_c vs $\chi_0(T_c)$ plot, as required by Eq. (4). In any case, these workers derived values of 1.63×10^3 mole/emu and 0.11 eV for α and J, respectively. Brill,¹⁵ working with alloys of 1-7-at. % Fe in Ag-Pd, compared his μ_e values with Eq. (5) and found that he could fit his data with $\alpha = 0.90 \times 10^3$ mole/emu at 333 K and 0.85×10^3 mole/emu at 386 K. Longworth¹⁰ also obtained rough agreement with Eq. (4) for Au-Pd(Fe) but he had to use $\chi_0(T_c)$ values appropriate to Ag-Pd, since no measurements on Au-Pd were available.

Figure 10 shows T_c/c for all our samples except those containing 6-at. % Fe. The host susceptibility x_0 was measured on an assortment of Au_xPd_{1-x} materials, between 4.2 and 300 K. In certain cases, the data had to be corrected because of the presence of a small concentration (of order 100 ppm) of unwanted magnetic impurities. Our magnetic and Mössbauer data are included. along with some T_c data of Longworth¹⁰ and Crangle, ${}^{26(a)}$ the latter relating to x = 0 [Pd(Fe)]. The straight line in the figure was drawn so that it passed through the origin, and the values for α and J obtained with Eqs. (4) and (7) are $\alpha = 1.80 \times 10^3$ mole/emu and J = 0.12 eV. These are similar to the above-mentioned values for the Ag-Pd(Fe) system. Although there is considerable scatter in the data of Fig. 10, the results seem to give additional qualitative support to the TSDW theory.

There are some problems, however, in reconciling the TSDW theory with all of our data. For example, Fig. 11 shows that T_c increases approximately as the square of the Fe concentration for the nominal x = 0.25 and x = 0.50 samples, at least for c between 0.02 and 0.06. Equation (4) obviously gives $T_c \propto c$. It might be argued that c is so large in our samples that



FIG. 10. Test of TSDW theory showing dependence of ordering temperature on host susceptibility at $T_{\rm c}$ Data of Longworth (Ref. 10) and Crangle [Ref. 26 (a)] are included. Data from our 6-at. %-Fe samples are not included on this graph.

Fe pairs or clusters are important, and that at much lower Fe concentrations the predictions of Eq. (4) would be fulfilled. That this is not the case in Pd(M) alloys (M = Fe, Co, Mn), however, has been shown by Nieuwenhuys, who demonstrates that T_c is approximately proportional to c^2 for $0.001 \le c \le 0.01$.² The inevitable conclusion is that the TSDW theory does not apply to any of the alloys: Pd(M), Au-Pd(Fe) or Ag-Pd(Fe), for magnetic-impurity concentrations of the order of one atomic percent.



FIG. 11. Log-log plot of ferromagnetic or spin-glass ordering temperatures as a function of Fe concentration, for $(Au_xPd_{1-x})_{1-c}Fe_c$ samples with nominal Au concentrations as shown. Note the change in c dependence between the ferromagnetic and spin-glass samples.

Although the above discussion casts doubt on the validity of Eqs. (4)-(6) as applied to our alloys, it is interesting to ask whether the TSDW theory could be correct in its description of the local-moment-conduction-electron coupling [Eqs. (5) and (6)], and be incorrect in the "interimpurity" coupling aspects as described by Eq. (4). After all, it is not unreasonable that there could be two exchange constants in the problem, α and γ , where γ is the molecular-field coefficient describing the interimpurity coupling.

Equations (5) and (6) of the TSDW theory are tested in Fig. 12. It can be seen that μ_s is, in fact, linear in $\chi_0(T_c)$ but that μ_e seems to be varying more slowly with χ_0 . Nevertheless, if one computes values based on the lines shown in Fig. 12, the results are $\mu_e = 1.49 \times 10^3$ mole/emu, $J_e = 0.096$ eV, and $\alpha_s = 1.80 \times 10^3$ mole/emu, $J_s = 0.12$ eV, where the subscripts refer to values obtained from effective- or saturation-moment data. The J_s value, it will be recalled, is identical with that obtained from Fig. 10.

Since μ_e is not truly linear in χ_0 , a fit was made to the equation $\mu_e = \mu_e^0 + a \chi_0^m$. The data do fit this equation well with

 $\mu_c^0 = [(s+1)/s]^{1/2} \mu_s^0 = 5.5 \mu_B (s = \frac{3}{2})$,

and with m = 0.5. It is not clear to us whether there is anything fundamental about this $\chi_0^{1/2}$ dependence.



FIG. 12. Dependence of effective moment and saturation moment on host susceptibility X_0 or $X_0(T_c)$, respectively. The μ_c and μ_s values are taken from Table II.

Another interesting question to be asked in regard to the foregoing is whether α or J should be independent of the Au concentration x. On the face of it, it would seem that the answer is negative because, even if a common band or virtual crystal were assumed, the exchange interaction in Au(Fe) is not necessarily equal to that in Pd(Fe). Suppose that we write phenomenological equations for μ_e and μ_{yy} , in analogy with Eqs. (5) and (6), viz.,

$$\mu_{e} = g \,\mu_{B} [s \,(s+1)]^{1/2} (1+\xi_{e}) \quad , \tag{8}$$

$$\mu_s = g \,\mu_B s \left(1 + \xi_s\right) \quad , \tag{9}$$

where ξ_e and ξ_s represent the conduction-electron contribution to the effective moment and saturation moment, respectively. Since it is well known in Pd(Fe) that the *bare* localized moment corresponds to a spin of $\frac{3}{2}$ (or 2),² it is reasonable to define the polarization cloud contributions as in Eqs. (8) and (9). ξ_e and ξ_s are plotted in Fig. 13(a). If we now define *concentration-dependent*-molecular-field coefficients δ_e and δ_s as

$$\delta_e \equiv \xi_e / \chi_0 \quad , \tag{10}$$

$$\delta_s \equiv \xi_s / \chi_0(T_c) \quad , \tag{11}$$

we obtain the results shown in Fig. 13(b). Implicit in Eqs. (8)-(11) is the idea that the giant polarization cloud magnitude is proportional to the *average* host susceptibility. This is tantamount to adopting a common band model in which local environment effects are completely ignored. Are the results of Fig.



FIG. 13. (a) Dependence on Au concentration of conduction-electron contribution to effective moment and saturation moment, as defined by Eqs. (8) and (9). (b) Dependence on Au concentration of molecular field coefficients as obtained from Eqs. (10) and (11).

13(b) for $\delta_e(x)$ and $\delta_y(x)$ reasonable? In a sense they do not seem to be because the δ values increase with x, whereas we know that the ferromagnetic localmoment-conduction-electron coupling is gradually losing its strength as x increases. In fact, for x = 1, the Au(Fe) case, J in the sd Hamiltonian is negative, and has a magnitude of order 1.7 eV according to Steiner et al. $\frac{26(a)}{a}$ What appears to be needed in the Au_xPd_{1-x} (Fe) system is a change in sign of J as x increases. This had already been suggested²⁷ for the analogous system $Cu_x Pd_{1-x}$ (Fe), in which the Kondo effect in Cu(Fe)-which requires a negative J-is lost as Pd is added to the host, even though Fe retains its localized moment for all x. Kondo²⁸ discusses how the sign of J is determined by a competition between the Zener sd exchange coupling, which can be positive, and the Anderson sd coupling which is negative. Since very little work has been done on ab initio calculations of J values in real binary alloys such as Cu(Fe), it is not possible to guess how J should vary in something as complicated as a disordered ternary alloy such as $Au_xPd_{1-x}(Fe)$.

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There is one further aspect of Fig. 13 which is worthy of comment. This is that $\delta_e > \delta$, and $\xi_e > \xi_s$. The latter inequality, in particular, indicates that the giant polarization cloud as measured in the paramagnetic state is larger than that measured in the ferromagnetic state. If anything, one would expect the reverse since at high temperatures the thermal fluctuations could be expected to break up some of the ferromagnetic coupling between the Fe local moment and the induced-polarization cloud, especially on its extremity. We can compare the magnitude of the totalspin cluster, Fe plus host neighbors, by comparing μ and $gS\mu_B$ values obtained from Table II. The result is shown in Fig. 14 in which it can be seen that the effective spin S of the total spin cluster appears larger



FIG. 14. Comparison of total cluster moment (bare Fe plus polarization cloud) as obtained from saturation moment data and paramagnetic moment data (Curie-Weiss fit, see text).

in the paramagnetic state than in the ferromagnetic state. We believe that the most likely explanation for this is that the Curie constants, from which μ_e and S values are derived, are too large as a result of some close-neighbor-ferromagnetic Fe-Fe interactions. Window²² has discussed how this can occur when $kT < J_{nn}$ (nn: near neighbor). Therefore, in Figs. 12 and 13, the data and interpretation for μ_{3} , ξ_{3} , and δ_{3} ought to be more correct than for the corresponding quantities derived from the paramagnetic data. This also could be related to the above mentioned linearity of μ_{λ} and the nonlinearity of μ_{e} in Fig. 12.

B. Nature of the coupling in the ferromagnetic alloys

We have argued in Sec. IV A that the TSDW theory is inadequate because it implies $T_c \propto c'_s$, whereas for our alloys, and also for Pd(Fe), Pd(Mn), Pd(Co), $T_c \propto c^2$. Most of the theories of ferromagnetic ordering in alloys, including for example, that of Sherrington and Southern (SS),²⁹ also give $T_c \propto c$. Sherrington and Southern discuss the competition between the ferromagnetic and spin-glass ordering in magnetic alloys and derive the following expression for T_c

$$T_{c} = \frac{s(s+1)}{3k_{B}} \tilde{J}_{0} \left\{ 1 + \left[1 - \left(\frac{\tilde{J}}{\tilde{J}_{0}} \right)^{2} \frac{3}{s(s+1)} \right]^{1/2} \right\} , \qquad (12)$$

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where \tilde{J}_0 is the average strength, and \tilde{J} the fluctuation magnitude, of the Heisenberg exchange coefficient. Assuming that $\tilde{J}/\tilde{J}_0 \ll 1$ gives

$$T_{c} = [s(s+1)/3k_{B}]\tilde{J}_{0} , \qquad (13)$$

and since

$$\tilde{J}_0 = \sum \left\langle J(R_1 - R_1) \right\rangle \equiv c j_0 \quad , \tag{14}$$

the ordering temperature is proportional to c in this theory as well. Since magnetic coupling of single spins of concentration c leads to $T_c \propto c$, it is tempting to suppose that $T_c \propto c^2$ implies magnetic coupling of *pairs* of spins. There is evidence that this is in fact true for dilute Cu(Fe) alloys.³⁰ The coupling of the Fe moments and their associated giant polarization clouds (hereafter called spin clusters) leads to a consideration of a statistical model in which the number of ferromagnetically coupled spin clusters is \overline{z} , which is a function of c. Then, instead of Eqs. (13) and (14), we have

$$T_{c} = [s(s+1)/3k_{B}]\bar{z}(c)j_{0} , \qquad (15)$$

where j_0 is the average exchange between spin clusters. In order to compute $\overline{z}(c)$ some assumptions have to be made about the range of the coupling between the Fe sites. Now it is known that the giant polarization clouds involve some 200 sites in the vicinity of a given Fe atom in Pd(Fe).³¹ Suppose we hypothesize that \bar{z} equals the concentration of Fe atoms which are located within the polarization clouds of *one* or more other Fe atoms. Thus $\bar{z}(c)$ is the concentration of ferromagnetically coupled spin clusters containing two or more Fe atoms; we exclude "isolated" spin clusters. The question is to see whether such an approximation will give through Eq. (15) the correct concentration dependence of T_c . Using standard statistical ideas,³⁰

$$\bar{z} = 1 - c (1 - c)^{\lambda}$$
, (16)

where λ here denotes the number of sites in the vicinity of a given Fe atom, which if occupied by another Fe atom, will be ferromagnetically coupled to the initial one. [$\lambda = 200$ for Pd(Fe)]. Figure 15 shows a calculation of $\overline{z}(c)$ for λ values of 200, 100, and 50. It can be seen that for $\lambda = 200$, \overline{z} and T_c are proportional to c^2 for $10^{-3} \le c \le 10^{-2}$, and that \overline{z} and T_c are approximately proportional to c for $c \ge 10^{-2}$. This curve in fact is very similar to the data shown by Nieuwenhuys² for Pd(Fe), Pd(Co), and Pd(Mn). Nieuwenhuys also calculated $T_c(c)$ based on the idea that $T_c \propto J_{int}(r)$ and $r \propto c^{-1/3}$; this amounts to assuming that the strength of the interaction between the giant moments is proportional to their overlap. In any case, the curve obtained by Nieuwenhuys is very similar to that shown for $\lambda = 200$ in Fig. 15. The curve for $\lambda = 50$ maintains a c^2 dependence to a somewhat higher concentration. Between c = 0.02 and 0.06,



FIG. 15. Dependence on the Fe concentration c of the number of ferromagnetically coupled Fe atoms as calculated by Eq. (16). \overline{z} is proportional to the ordering temperature according to Eq. (15).

 $T_c \propto \overline{z} \propto c^{1.4}$, which is still a somewhat slower variation than we observe in the Au-Pd(Fe) alloys between 2and 6-at.% Fe. Presumably by decreasing λ still further it would be possible to obtain a c^2 behavior even up to ~6-at.% Fe.

Now it is reasonable that λ in Au_xPd_{1-x} (Fe) should be smaller than it is in Pd(Fe), because one expects the range of the coupling to decrease as x increases. However, it is not at all clear what the functional dependence of $\lambda(x)$ should be, since this ought to depend in a complicated way on the electronic structure of Au_xPd_{1-x}.

Summarizing, we have shown qualitatively how a simple model of the coupling of the giant spin clusters can lead to a $T_c \propto c^2$ behavior in Pd(Fe), Au_xPd_{1-x}(Fe), and similar alloys. The discussion also suggests that it will be very difficult indeed to theoretically calculate the dependence of T_c on c in a fundamental way in a disordered alloy such as Au_xPd_{1-x}(Fe).

C. Transition to spin-glass ordering in Au-rich alloys

We have seen in the above discussion that for Pd(Fe) alloys there exist giant polarization clouds which interact and lead to ferromagnetism. As Au is added, the polarization clouds decrease in size and magnitude. The natural question that arises is: is there a reasonable explanation, in terms of the electronic structure of Au_xPd_{1-x} , for the change in character of the magnetic coupling at $x \approx 0.5$. Unfortunately, there have been no coherent-potentialapproximation (CPA) calculations for $Au_{x}Pd_{1-x}$. However, Stocks et al.⁶ have performed CPA calculations for $Ag_{x}Pd_{1-x}$ for x = 0.2, 0.4, 0.6, 0.7, and 0.85. It is reasonable to expect that CPA calculations for. Au_xPd_{1-x} would lead to results quite similar to those of $Ag_x Pd_{1-x}$. The results of Stocks *et al.* agree rather well with the photoemission studies of Norris and Myers³² and Hüfner et al., ³³ and show that a virtual bound state develops on the Pd atoms, which grows increasingly as the Pd concentration increases from zero. In particular, the density of states curves show that between 40 and 60 at. % Ag, the states at the Fermi level change from being composed almost completely of Pd d states, to Ag s states. In fact, the theoretical electronic specific-heat coefficient $\gamma(x)$ shows that $\gamma(x) \approx \text{const for } 0.5 \le x \le 1$, and a sharp rise for x < 0.5. Assuming the above mentioned similarity between Au-Pd and Ag-Pd, then, one can say that as x increases above 0.5 in Au_xPd_{1-x} , the states near the Fermi level lose their d character, which completely eliminates the local "pockets of ferromagnetism," i.e., the giant polarization clouds. Under these circumstances, the conduction electrons (of s-wave nature) scatter from the Fe impurities in a way that can be described by the Friedel model which

leads to Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling between the bare Fe moments. Since this coupling is rather long range and oscillatory, the normal spin-glass or mictomagnetic properties result for x > 0.5. In particular, Fig. 11 shows for $x \approx 0.75$, that the spin-glass ordering temperature T_{sg} is increasing as c^m , where $m \approx \frac{2}{3}$. This is similar to the behavior of Au(Fe) and other canonical spin glasses for which, depending upon concentration, *m* varies from $\frac{1}{2}$ to $\frac{2}{3}$.¹

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We have estimated the interimpurity coupling strength in the spin-glass samples ($x \approx 0.75$ and x = 1) in two ways, one based on the field dependence of M(H) along with the theory of Larkin,³⁴ and the other based on the spin-glass ordering temperature along with the theory of Sherrington and Southern.²⁹

Following the convenient notation of Hou and Coles,³⁵ the theory of Larkin gives, for $g\mu_B H >> kT$ and $g\mu_B H >> nV_0$,

$$M(H) = g \mu_B sn \left(1 - \frac{2(2s+1)nV_0}{3g \mu_B H} \right) , \qquad (17)$$

$$V(r) = \frac{V_0(\cos 2k_F r)}{r^3} , \quad k_F r >> \pi , \quad (18)$$

$$V_0 = 9\pi^2 J^2 s \left(s + 1\right) / 32\sqrt{2} E_F k_F^3 \quad , \tag{19}$$

where M(H) is the magnetization, *n* the impurity concentration, V(r) the spatial dependence of the RKKY interaction, V_0 the amplitude of the RKKY interaction, k_F the Fermi wave vector, and the other symbols have their usual meanings. A plot of M vs H^{-1} , with data taken for the $c \simeq 0.02$ and x = 0.75and 1.0 samples, was linear in H^{-1} as required by Eq. (17). However, the $H^{-1} = 0$ values of *M* correspond to gs values of 1.15 and 2.0 for the x = 1 and x = 0.75samples, respectively. Assuming reasonable values for s and g $(\frac{3}{2}$ and 2), these extrapolated values should be 3. It seems likely that the major reason for this inconsistency between experiment and theory is that the Fe concentration ($c \simeq 0.02$) is so large that there is a considerable number of close-neighborantiferromagnetic interactions which are so strong that they are not significantly broken up even in fields of about 100 kOe. If this is true it should be possible to modify Eq. (17) by replacing *n* by $\frac{2}{3}n$ for x = 0.75 and by replacing *n* by (1.15/3)n for x = 1, and thus to obtain an approximate value for the RKKY coupling strength V_0 and the exchange constant J. This procedure amounts to treating only the weakly interacting Fe spins by the Larkin formula. The slope of the M vs H^{-1} data give V_0 values of 1.7×10^{-37} erg cm³ and 0.78×10^{-37} erg cm³ for the x = 1.0 and 0.75 samples, respectively. Then, using free-electron parameters for E_F and k_F , Eq. (19) gives sd coupling constants of |J| = 0.38 and 0.25 eV, for the x = 1.0 and 0.75 samples, respectively. The 0.38eV value for the Au-2-at. %-Fe sample is considerably smaller than the 1.7 eV value determined from the Mössbauer effect by Steiner *et al.*,^{26(h)} but this is not too surprising for two reasons. One is that hyperfinefield estimates of J often differ from dc measurements for reasons discussed by Narath³⁶ and Heeger.³⁷ Secondly, Liu and Smith have shown that V_0 is a strong function of impurity concentration in Au(Fe) alloys.³⁸ For example, they obtain V_0 values of 4.5×10^{-36} and 1.03×10^{-36} erg cm³ for 0.017 and 0.6at. %-Fe samples, respectively. Thus, our value of 1.7×10^{-37} erg cm³ for c = 0.02 is consistent with the trend of decreasing V_0 with increasing c. Liu and Smith attribute this behavior to self-damping of the RKKY oscillations by increased impurity scattering.

The second method for estimating the coupling strength in the spin-glass samples employs the expression of Sherrington and Southern for the spin-glass ordering temperature²⁹

$$T_{sg} = (\tilde{J}/3k_B) \{ [s(s+1)]^2 + \frac{1}{2} [s(s+1)] \}^{1/2} , \qquad (20)$$

where \tilde{J} measures the fluctuation in the exchange coupling. The above expression gives $\tilde{J} = 7.6 \times 10^{-4}$ eV and 6.2×10^{-4} eV for the x = 1 and x = 0.75 samples, respectively. To compare these with the values obtained from the Larkin expression, it must be noted that \tilde{J} corresponds to $\langle V_0/r_{il}^3 \rangle$ in the RKKY formalism. Thus, to calculate \tilde{J}_L from the Larkin expression, we have

$$\tilde{J}_L \equiv \langle V_0/r_{\mu}^3 \rangle = V_0 16 \pi c/3a^3$$

where *a* is the lattice constant. We thus obtain values for J_L of 5.4×10^{-4} eV and 2.4×10^{-4} eV for the x = 1.0 and 0.75 samples. These values are similar in magnitude to those estimated above from the Sherrington and Southern expression.

V. SUMMARY AND CONCLUSIONS

The major results of this study are as follows. (i) The Takahashi-Shimizu-Doniach-Wohlfarth theory appears to be incapable of properly describing

the interimpurity coupling that leads to magnetic ordering in the Pd-rich Au_xPd_{1-x} (Fe) alloys. Presumably, this is true also for similar alloys such as Ag_xPd_{1-x} (Fe).

(ii) If we assume that the exchange parameter describing the local-moment-conduction-electron coupling is independent of Au concentration, and assume that the TSDW theory correctly describes this coupling, we obtain a value of $J \simeq 0.12$ eV from the μ_x vs χ_0 data.

(iii) We have derived from the $\mu_{n}(x)$ data the concentration dependence of the giant polarization cloud. Assuming that the magnitude of this cloud is porportional to the *average* host susceptibility, we have derived a *concentration-dependent* exchange coefficient that increases as x increases. It is not clear whether this coefficient is meaningful because it implies a common band model and ignores all localenvironment effects. This is a question which warrants theoretical work because the site dependence of J in a disordered alloy presumably is central to the problem of properly describing ferromagnetism in disordered alloys.

(iv) The quadratic concentration dependence of the ferromagnetic ordering temperature in our alloys, as well as other exchange-enhanced alloys like Pd(Fe), Pd(Mn), etc., is not understood in terms of any theory. We have shown that a phenomenological model—in which one assumes that all Fe atoms, within one or more neighboring giant polarization clouds, are coupled together ferromagnetically—is capable of qualitatively describing the concentration dependence of T_c of the known exchange-enhanced alloys from about 0.1 to 10 at.% of magnetic impurity. However, in a ternary alloy like Au Pd₁ (Fe), it is impossible to estimate the range of the coupling without measurements such as neutron diffraction.

(v) The change from ferromagnetic to spin-glass

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ordering at about x = 0.5 seems to be connected with the fact that the states near the Fermi level change from *d*-like to *s*-like at this composition; this argument is based on the expected similarity of the electronic structure of Au_xPd_{1-x} to that of Ag_xPd_{1-x}, for which CPA calculations have been performed.

(vi) The two spin-glass samples (x = 1 and x = 0.75) can be understood in terms of the Sherrington-Southern theory which is based on fluctuations in the exchange coupling of the Fe spins. Estimates of the magnitude of the coupling were made with the Sherrington-Southern theory and these agreed reasonably well with those based on the Larkin theory for the high-field magnetization.

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