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ac susceptibility and electrical resistivity measurements on the spin-glass phase of *Pd*Mn

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Measurements of the ac susceptibility and electrical resistivity of 11 *Pd*Mn alloys containing between 5.5 and 10.45 at.% Mn are presented as a function of temperature from 1.4 to 20 K. The zero-field ac susceptibility exhibits a peak whose position and height is modified by the application of static biasing fields. These data, however, do not obey either the geometrical Ruderman-Kittel-Kasuya-Yosida (RKKY) scaling relationships or recent predictions based on a short-range model for spin-glasses. The incremental resistivity follows a linear temperature dependence at lower concentration and a $T^{3/2}$ limiting form at higher concentration. The range of validity of these dependences imply that they cannot originate from conduction-electron scattering simply from low-lying excitations. We conclude that existing theories do not adequately account for the processes occurring in *Pd*Mn alloys where the upper spin-glass state results from competing interactions between a long-range ferromagnetic component and a near-neighbor, short-range antiferromagnetic component. A detailed magnetic phase diagram has also been constructed which appears to suggest the possibility of a double transition, i.e., a reentrant ferromagnetic to spin-glass transition at low temperature. The experimental data do not support such implied behavior in this system.

I. INTRODUCTION

In two recent papers we reported the results of an investigation of the ac susceptibility and electrical resistivity of some dilute *Pd*Mn alloys containing between 0.5 and 2.5 at.% Mn,[1] and 3.0 and 5.0 at.% Mn, respectively.[2] At the lower concentrations studied, these alloys underwent a paramagnetic to predominantly ferromagnetic transition as the temperature was reduced, which was accompanied by a sharp change in slope in the incremental resistivity $\Delta\rho(T)$ and a power-law dependence of the ac susceptibility $\chi(h,t)$ in the vicinity of the Curie temperature T_c, viz,

$$\chi(0,t) \propto t^{-\gamma} , \tag{1}$$

$$\chi(h,t_m) \propto h^{1/\delta-1} , \tag{2}$$

as predicted by the scaling-law equation of state (in terms of the usual reduced temperature t and internal field h). Even below 2.5 at.% Mn, however, there was strong evidence of the influence of near-neighbor direct *d-d* overlap between Mn impurities (which is expected[3] to be antiferromagnetic in sign); such coupling caused a broadening of the internal field distribution[1,2] with an attendant smearing of the critical region and a reduction in the estimated value for the critical index δ.[4] Associated effects were observed in $\Delta\rho(T)$, which displayed an increased temperature dependence above the bulk ordering temperature that presumably resulted from the thermally induced breakup of the coupling between adjacent impurities experiencing a larger than average internal field.

The effects discussed above became more pronounced in the range 3.0 to 5.0 at.% Mn, reflecting the increasing occurrence of near-neighbor direct *d-d* overlap between the impurities. Indeed, for these alloys the smearing of the critical region resulting from the broadened internal field distribution was such that the power-law dependences given in Eq. (1) and (2) were no longer followed. In fact, at 5 at.% Mn, the zero-field ac susceptibility exhibited a sharp peak which was reduced in both magnitude and temperature by an applied field, while the incremental resistivity showed a smooth variation with temperature over the corresponding interval. This latter behavior is reminiscent of that displayed by many spin-glasses.[5]

In this paper, we report the detailed study of the ac susceptibility and electrical resistivity of alloys containing between 5.5 and 10.45 at.% Mn, which places them in this (upper) spin-glass phase. The latter phase originates from competing interactions between long-range ferromagnetic coupling (which derives from the modification of conventional local moment-induced conduction-electron polarization[6] by exchange enhancement effects[7]) and near-neighbor antiferromagnetic coupling via direct interimpurity *d-d* overlap. This situation thus contrasts with that existing in conventional spin-glasses where the oscillatory nature of the conventional conduction-electron polarization alone (the RKKY coupling) produces interactions of both signs. In particular, we were in-

terested in whether the elementary excitations in the *Pd*Mn alloys studied here yielded a temperature dependence for the conduction-electron scattering cross section which was similar to that observed in conventional spin-glasses, and secondly, how the "geometrical" scaling laws derived from the conventional RKKY coupling[8] were modified.

II. EXPERIMENTAL DETAILS

11 alloys containing from 5.5 to 10.45 at.% Mn in approximate steps of 0.5 at.% Mn were prepared by successive dilution of a 10.45 at.% Mn master alloy by arc melting. Analysis of the master alloy yielded a concentration of 10.21 ±0.25 at.% Mn. Details of the sample preparation and annealing procedures have been given in a previous paper,[1] which also contains a discussion of the ac susceptibility measurements (at 2.4 kHz with a driving field of 0.5 Oe rms) and the four-probe dc potentiometric technique for measuring the temperature-dependent sample resistivities. It should be noted, however, that while the relative values for the ac susceptibility of a particular alloy can be determined with high precision, absolute values are uncertain to typically ±10% due mainly to filling-factor uncertainties and nonuniform sample shapes.

III. RESULTS AND DISCUSSION

A. ac susceptibility

In Fig. 1, the ac susceptibility in zero applied field and in various small collinear biasing fields is displayed as a function of temperature for two alloys containing 6.0 and 9.0 at.% Mn, respectively. These curves typify the data that have been obtained in this concentration range, and both sets of data exhibit similar features to those reported for conventional spin-glasses. A detailed examination of the two sets of curves, however, reveal some differences; specifically at 6 at.% Mn, the zero-field ac susceptibility exhibits a relatively sharp peak around 3.6 K which is quite rapidly suppressed in both magnitude and temperature by an applied field, so that at 300 Oe the peak in the susceptibility now occurs around 2.9 K and is nearly 50% smaller than in zero applied field. In contrast, at 9 at.% Mn, the effect of an external field is not nearly so marked in its influence on both the height and position of the susceptibility maxima. Furthermore, the zero-field peak susceptibility decreases as the Mn concentration increases throughout the range examined — see Table I.

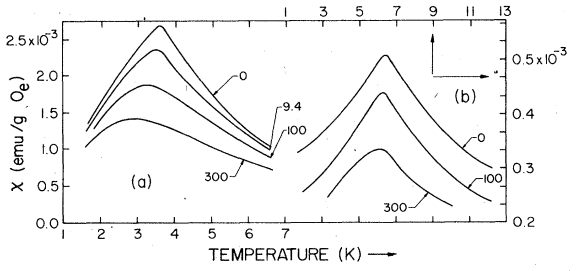

FIG. 1. ac susceptibility $\chi(H,T)$ (in emu/g Oe) for (a) Pd−6 at.% Mn and (b) Pd−9 at.% Mn. The numbers marked against each curve give the net static biasing field (in Oe). In the case of the 9 at.% Mn sample the vertical scale applies to the data taken in a biasing field of 300 Oe; each subsequent curve has been raised by two scale units (0.67×10^{-4} emu/g Oe) for clarity.

The "geometrical" scaling laws[8] based on the RKKY interaction and the consequent invariance of the product $c\langle r_{ij}\rangle^3$ (where c is the impurity concentration and $\langle r_{ij}\rangle$ the mean interimpurity separation) lead to the prediction of a universal behavior for $\chi(0,T/c)$. Table I indicates that such a behavior is not followed in the present system as $\chi(T\rightarrow 0)$ and $\chi(0,T_0)$ are not constant, nor does T_0 scale with c. However, following the discussion in the introductory section on the origin of the competing interactions (in particular, the near-neighbor antiferromagnetic component) which give rise to the spin-glass state under investigation here, this nonadherence to "geometrical" scaling was anticipated.

Recently, Abrikosov[9] has reviewed the properties of spin-glasses that result from *short*-range interactions, that is, systems in which the conduction-

TABLE I. Summary of the ac susceptibility data.

Alloy (at.% Mn)	T_0 (K)	$\chi(0,T_0)$ (10^{-3} emu/g Oe)	$\chi(0,T=1.5\text{ K})/\chi(0,T_0)$
5.5	3.15 ± 0.05	4.6 ± 0.5[a]	0.42
6.0	3.6 ± 0.05	2.7 ± 0.3	0.46
6.5	3.9 ± 0.05	2.0 ± 0.2	0.50
7.0	4.3 ± 0.05	1.7 ± 0.2	0.48
7.5	5.1 ± 0.05	0.74 ± 0.07	0.50
8.0	5.55 ± 0.05	0.44 ± 0.04	0.50
8.5	5.9 ± 0.05	0.39 ± 0.04	0.57
9.0	6.5 ± 0.05	0.37 ± 0.04	0.50
9.5	7.05 ± 0.05	0.31 ± 0.03	0.50
10.0	7.55 ± 0.05	0.26 ± 0.03	0.50
10.45	8.05 ± 0.05	0.29 ± 0.03	0.56

[a]Errors in the absolute value of the susceptibility are typically ±10% (see text). Note that for the sample sizes and ac driving fields used here, an error of $\pm 3\times10^{-5}$ emu/g Oe translates into an error of $\pm 1.5\times10^{-6}$ emu in the induced magnetization.

electron mean free path l is such that it satisfies the inequality $l\langle r_{ij}\rangle << 1$. In such systems at high temperatures, the spins are, of course, essentially isolated from each other, but as the temperature decreases, *near–neighbor* two-spin clusters first appear. Such clusters grow in size as the temperature is further reduced, and since each additional spin coupling to the cluster interacts predominantly with its closest neighbor, the spin arrangements within each cluster are initially collinear. This process continues until at temperature Θ the infinite chain forms at the percolation threshold, characterized by a susceptibility cusp. This approach contains many of the same features introduced previously by Smith[10,11] to discuss the spin-glass problem, except that the latter author considered the limit $l\langle r_{ij}\rangle >> 1$ when the RKKY interaction is of very long range, and the "geometrical" scaling predictions are recovered. While these percolation-based approaches treat the spin-glass problem in different limits of the product $l\langle r_{ij}\rangle$ with differing consequences, both agree on the following relationship involving the peak susceptibility $\chi(0,T_0=\Theta)$:

$$\chi(0,T_0)\,T_0 \propto c \quad . \tag{3}$$

The lack of agreement between the experimental data reported here and the above prediction has already been pointed out in the previous paragraph; in fact, the experimental data on *Pd*Mn in the range 5 to 10 at.% Mn exhibits the opposite trend to that given in Eq. (3) as the product $\chi(0,T_0)$. T_0 is observed to decrease with increasing Mn concentration.

It would thus appear that the features observed in the susceptibility of the *Pd*Mn system in which the (upper) spin-glass state is produced by a competition between long-range ferromagnetic coupling via the polarized *d*-band and short-range antiferromagnetic near-neighbor direct overlap, cannot be accounted for directly using existing percolation-based approaches based *solely* on either *long*-range or *short*-range interactions.

B. Electrical Resistivity

An extensive body of data exists on the transport properties of conventional spin-glasses.[12] In these systems the incremental resistivity $\Delta\rho(T)$ is observed to follow at $T^{3/2}$ limiting form at low temperatures while at higher temperatures (around that of the susceptibility maximum, T_0) a linear dependence is observed. This initial $T^{3/2}$ dependence in $\Delta\rho(T)$ has often been attributed to conduction-electron scattering inelastically from weakly damped, long-wavelength spin diffusion modes which characterize the low-temperature elementary excitations of spin-glasses of the long-range RKKY type.[13] In contrast, a similar recent calculation for spin-glasses formed by short-range interactions[9] yields a linear limiting temperature dependence for $\Delta\rho(T)$.

In Fig. 2 representative sets of incremental resistivity data from the 6, 8.5, and 10 at.% Mn alloys are presented as a function of temperature up to 20 K. These incremental resistivities were obtained simply by subtracting the measured pure Pd resistivity from that for the appropriate alloy, although at the impurity concentrations of interest here the correct matrix resistivity could be somewhat different from that of pure Pd due to changes induced in both the electronic band structure and the phonon dispersion curves by alloying. Further, this simple subtraction procedure does not take into account any nonmagnetic deviations from Matthiessen's rule.[14] The incremental resistivity curves that result show little structure. In the case of the 6 at.% Mn sample, within experimental error, $\Delta\rho(T)$ exhibits a linear temperature dependence from around 11 K to the lowest measuring temperature achieved in this experiment ($\sim$1.4 K). The coefficient of this linear decrease, listed in Table II, is close to that measured previously[2] for a 5 at.% Mn sample, and the data show no anomalous features in the vicinity of T_0 (indicated by the vertical arrow in Fig. 2). Between 5 and 7 at.% Mn, all the alloys we have studied exhibit this same behavior.

At 7.5 at.% Mn there is some slight deviation away from this linear temperature dependence at the lowest temperatures, and as can be seen from Fig. 2, such deviations become quite marked by 8.5 at.% Mn. Indeed at 8.5 at.% Mn, and above, these deviations from linearity are such that the low-temperature incremental resistivity follows a $T^{3/2}$ limiting form

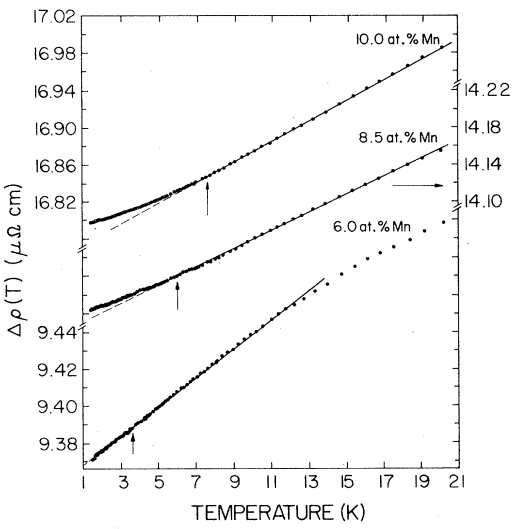

FIG. 2. Incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$ cm) plotted against temperature (in K) for the samples containing 6, 8.5, and 10 at.% Mn, respectively. The vertical arrows mark the position of the susceptibility maxima.

TABLE II. Summary of parameters from the resistivity data.

Alloy (at.% Mn)	$\Delta\rho(T=0)$ ($\mu\Omega$ cm)	Coefficient of the linear term ($\mu\Omega$ cm K^{-1})	Coefficient of the $T^{3/2}$ term ($\mu\Omega$ cm K$^{-3/2}$)
5.5	8.61	0.008(4)	. . .
6.0	9.37	0.008(0)	. . .
6.5	10.38	0.007(6)	. . .
7.0	11.25	0.008(4)	. . .
7.5	12.35	0.008(8)	. . .
8.0	13.18	0.009(0)	. . .
8.5	13.98	0.009(5)	0.002(9)
9.0	15.28	0.010(4)	0.002(7)
9.5	16.12	0.010(8)	0.002(7)
10.0	16.79	0.011(0)	0.002(7)
10.45	18.11	0.011(2)	0.002(7)

with tolerable accuracy, as shown in Fig. 3. Within experimental error we find that the coefficient of this $T^{3/2}$ term does not change with concentration between 8.5 and 10.45 at.% Mn, although its range of validity climbs from around 6.3 K at 8.5 at.% to about 7.7 K at 10.45 at.% Mn.

While existing theories variously predict that[9] $\Delta\rho(T) \propto T$ or[13] $\Delta\rho(T) \propto T^{3/2}$ at low temperatures in spin-glasses, we do not believe that these theories correctly identify the origin of those processes dominating the resistivity in *Pd*Mn spin-glasses, for the following reasons: Calculations of the resistivity based on models of systems dominated by either short-range[9] or long-range[13] interactions yield the temperatures dependences listed above by considering conduction-electron scattering from the appropriate thermally generated low-lying excitations out of the ground state. In the case of alloys containing 7 at.% Mn, or less, the measured linear temperature dependence in $\Delta\rho(T)$ extends from temperatures well below T_0 to temperatures well above T_0, and so it would appear to arise as a result of scattering from a far wider spectrum of excitations than simply those at low energy. The same conclusions can be drawn from the data at higher concentrations where a $T^{3/2}$ form is observed, extending to temperatures on the order of T_0. In conventional spin-glasses[12] this latter form persists to typically 15–30% of T_0 and so its association with low-lying excitations seems plausible; paradoxically in the *Pd*Mn system it appears to span a temperature interval up to 90% of T_0 in the more concentrated alloys, yet it cannot be resolved at temperatures which are a far smaller fraction of T_0 at lower concentrations.

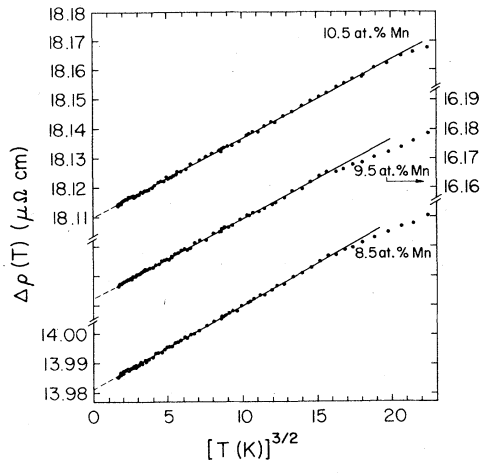

FIG. 3. Low-temperature incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$ cm) plotted against $T^{3/2}$ (in K$^{3/2}$) for the 8.5, 9.5, and 10.45 at.% Mn samples.

Existing theories do not appear capable of accounting for such differences in behavior and hence, as with the susceptibility data, we must conclude that such theories are based on models which are not appropriate for *Pd*Mn spin-glasses.

C. Phase Diagram

Figure 4 summarizes our data on the *Pd*Mn system, covering the concentration range 0.5 to 10.45 at.% Mn. While a consensus now exists on that portion of this diagram below about 2.5 at.% Mn, there is considerable ambiguity surrounding existing higher concentration data, particularly in the spin-glass regime. Such ambiguities arise from two sources; first, uncertainties in the Mn content, specifically alloys

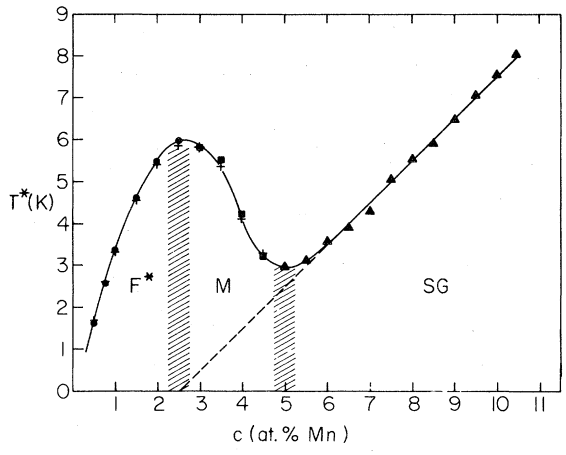

FIG. 4. Summary of the phase diagram for the *Pd*Mn system, showing the estimated ordering temperature T^* (in K) plotted against the Mn concentration c (in at.%). The three regions are designated F^* — predominantly ferromagnetic, M — mixed ordering, and SG — spin-glass. The symbols represent (i) ● and + are Curie temperatures estimated from ac susceptibility and resistivity measurements, respectively; (ii) ■ and + are pseudocritical temperatures obtained from the ac susceptibility and electrical resistivity data in the mixed ordered region, and (iii) ▲ are the temperatures of the zero-field ac susceptibility maxima.

with the same nominal concentration are reported as having marked differences in their residual resistivities. Secondly, some estimates of the susceptibility peak temperature T_0 in the spin-glass regime have been made in the presence of static applied fields of several hundred oersted. In regard to the first point, the residual resistivies listed in Table II of this paper and in similar tables in Ref. 1 and 2, when plotted against Mn concentration, yield a good straight line of slope 1.62 ± 0.05 $\mu\Omega$ cm/at.% Mn with little scatter. For the second point — the influence of static biasing fields — in discussing the susceptibility data it has already been pointed out that such fields result in a suppression of the temperature at which the susceptibility maximum occurs.

Thus the phase diagram that has been constructed — Fig. 4 — is, we feel, more reliable than any currently postulated for the *Pd*Mn system — particularly in view of the two points stressed above. This is an important assertion as a result of its implication for the behavior of this system between 3 and 5 at.% Mn. As can be seen from Fig. 4, a plausible straight-line extrapolation of the temperatures T_0 of the zero-field susceptibility maxima yields an intercept around 2.5 at.% Mn. Similar extrapolations in the *Au*Fe (Refs. 15 and 16) and *Pd*(Fe, Mn) (Refs. 17 and 18) systems have led to speculations regarding the possibility of double transitions; a paramagnetic to quasiferromagnetic transition at a temperature corresponding to the upper line, followed by a second transition into a spin-glass state at a temperature corresponding to an extrapolation from the spin-glass regime. Model calculations have also suggested such possibilities.[19] While we do not wish to comment on the various experiments and their interpretation in the two systems mentioned above, we would like to point out that double transitions with the features discussed above do not exist at intermediate concentrations in the *Pd*Mn system. It is certainly true that alloys containing 3 to 5 at.% Mn exhibit a complicated behavior with double peaks appearing in the ac susceptibility measured in small biasing fields.[2] The peak occurring at higher temperature moves progressively upwards in temperature with increasing applied field, although its height decreases; the estimated position of this peak in zero field (along with an associated anomaly in the incremental resistivity) has been used to construct the upper line in Fig. 4, and although these features resemble those obtained in ferromagnetic alloys,[1] we have suggested that this line does not represent a true ferromagnetic transition for reasons discussed in detail previously.[2] The second peak, at lower temperature, moves rapidly downwards in increasing applied fields, and consequently, while its position in zero field is difficult to estimate precisely, we can nevertheless state equivocally that it does *not* coincide with the extrapolated line. It lies far closer to the *upper* line. As we have pointed out previously, this second peak originates in the vicinity of the principal maximum in the zero-field ac susceptibility. From the data that have been presented in this paper, we imply that while the "anisotropy" responsible for the principal zero-field ac susceptibility maxima has not been specified, it does not have any direct connection to processes causing the freezing in the spin-glass state.

IV. SUMMARY AND CONCLUSIONS

The ac susceptibility and electrical resistivity of several *Pd*Mn alloys containing between 5.5 and 10.45 at.% Mn have been measured. The data obtained exhibit several features which superficially resemble the behavior reported for conventional spin-glasses, however, detailed comparisons lead us to suggest that existing models do not adequately represent the processes occurring in this system.

A detailed magnetic phase diagram has been constructed, which suggests the possibility of reentrant behavior at low temperatures. The experimental data, however, do not support such implied behavior.

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