Palladium-Iron: A Giant-Moment Spin-Glass at Ultralow Temperatures

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We report on low-frequency ac susceptibility measurements on Pd doped with 2.2, 6.8, 11, and 100 at. ppm Fe at temperatures between 79 μK and 24 mK and in fields of less than 1 mG at 3.8 G. The samples show typical spin-glass behavior with a ratio of freezing temperature to Fe concentration $T_f/x \simeq 83$ μK/at. ppm Fe. The effective moment determined from the Curie constant at $T \gtrsim 2T_f$ is $10\mu_B$ per Fe atom.

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The only *d* elements which have shown neither superconductivity nor magnetism up until now are palladium and platinum. Both have a high *d*-electron density of states at the Fermi energy and rather strong electron-phonon coupling; therefore one might expect them to be good superconductors. Instead, the high density of electron states and the resulting tendency to magnetism seem to be detrimental for singlet superconductivity in both elements.

In extending our search for the ground state of metallic elements at ultralow temperature we have investigated very dilute *Pd*-Fe as well as Pt-Ir alloys. Because of the strong tendency towards magnetism an investigation of the influence of low concentrations of magnetic impurities on the properties of Pd seems to be appropriate before searching for the ground state of "pure" palladium.

Former measurements of the susceptibility of *Pd*-Fe showed this to be a system of local moments with about $10\mu_B$/Fe atom.[1] This giant moment arises from the polarization of the Pd neighbors around the iron atoms. The percolation limit for ferromagnetism of the giant moments is about 0.1% Fe. Chouteau and Tournier[2] had observed deviations from the high-temperature Curie-Weiss behavior in the susceptibility of *Pd*-Fe with lower iron concentrations. Measurements by Webb, Crabtree, and Vuillemin[3] as well as theoretical predictions[4] have indicated that dilute *Pd*-Fe should be a spin-glass. In this Letter we report our results of low-frequency ac susceptibility measurements at ultralow temperatures on Pd with 2.2 to 100 at. ppm Fe. We find typical spin-glass behavior for these extremely dilute samples with concentrations and freezing temperatures nearly 3 orders of magnitude smaller than reported for previous experiments.

Our experiments were performed in the Jülich two-stage nuclear degmagnetization refrigerator.[5] One end of each sample was attached by a 1.4-mm Cu screw to a Cu cold finger mounted on the Cu nuclear stage. Pickup coils were wound directly on the free ends of the samples. The ac susceptibility of each sample could be measured independently by applying fields of 45 μG at 3 to 86 Hz. dc magnetic fields up to 4 G could be applied by a separate coil. Details of the field shielding to below 1 mG at the samples and of the SQUID ac susceptibility measurements have been published before.[6] The temperature was measured by pulsed NMR on Pt wires which were mounted on a second cold finger.[5] The samples had typical dimensions of $2\times4\times7$ mm^3 and consisted of a few crystallites. The skin depth for our experimental conditions was of order 1 mm. The samples were prepared from a 1-mm-thick Pd wire from Johnson-Matthey. We took this material as our most dilute sample, containing 2.2 at. ppm Fe. The samples were produced by high-frequency melting. They were annealed for 5 h at 1300 °C in 10^{-10} Torr. Their residual resistivity as well as the Fe concentration measured by mass spectroscopy are given in Table I. The concentration of the other 3*d* impurities was less than 1 ppm. For a second determination of the concentration of Fe in our samples we measured their susceptibility in 5 kG above 2 K. For the analysis we assumed that Fe is the dominant magnetic impurity and —following the results of Clogston *et al.*[7] for alloys with 1% Fe—that this impurity carries a moment of $11\mu_B$. The iron concentrations determined under these assumptions (see Table I) agree rather well with the iron concentrations determined from the mass spectroscopy which we take for the further analysis.

Figure 1 shows the 3-Hz susceptibility of our samples at temperatures below 5 mK. In zero field each sample shows a peak in the ac susceptibility at a temperature T_f which is proportional to the iron concentration. We find $T_f/x \simeq 83$ μK/ppm (see Table I) which is substantially smaller than the corresponding ratio in the ferromagnetic range at $x \gtrsim 0.1\%$. The data were taken while cooling and warming in zero field without showing any hysteresis. On the low-temperature side of its maximum, the susceptibility decreases rapidly without

TABLE I. Properties of the investigated samples (for details see text).

Sample	Residual resistivity ratio	Fe concentration (at. ppm) from mass spectroscopy	Fe concentration (at. ppm) from high-T susceptibility	T_f (mK)	T_f/x_{Fe} (μK/ppm)	μ/μ_B
2.2-ppm UHV anneal	1285	2.2 ±0.7	1.8	0.19	89	9.3
2.2-ppm air anneal	3360	2.2 ±0.7	1.8	0.17	77	...
6.8-ppm UHV anneal	993	6.8 ±0.8	7.8	0.54	80	10.3
6.8-ppm air anneal	1610	6.8 ±0.8	7.8	0.44	64	...
11-ppm UHV anneal	893	11 ±4.6	13.7	0.90	82	10.2
11-ppm air anneal	1352	11 ±4.6	13.7	...	...	...
11-ppm air anneal/rolled	231	11 ±4.6	13.7	0.86	78	...
100-ppm UHV anneal	...	...	...	9.0	90	...

saturating even at the lowest temperature of these runs, 79 μK. For the three most dilute samples the height of the susceptibility peak is about two orders of magnitude smaller than the estimated ferromagnetic limit $1/N$ (N: demagnetization factor). Figure 1 also demonstrates that the peak of the 100-ppm sample is considerably larger than those of the more dilute samples; the height of the susceptibility peak depends on the freezing temperature, which is a typical spin-glass behavior.[8] Applying fields B of a few gauss results in a strong depression and rounding of the susceptibility maximum (see Fig. 1). Plotting the ac susceptibility measured at constant B/x as a function of T/x results in a universal curve. The data also indicate that the susceptibility below the maximum is slightly larger if the sample is cooled in a field of 3.8 G. This small hysteresis in the magnetization becomes more obvious with increasing iron concentration. All these observations are typical for a spin-glass and distinctly different from ferromagnetism or antiferromagnetism.

Above a temperature about twice the temperature of the susceptibility maximum, the susceptibility can be represented by a Curie law. To determine the Curie constant we have plotted the reciprocal value of the susceptibility (minus the susceptibility background measured at higher temperatures) as a function of temperature. The resulting straight lines go through the origin indicating that the mean interaction between the magnetic moments is zero. This is reasonable if the interaction results from the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, which oscillates nearly symmetrically about zero and gives a zero net value because of the large distance of 100 and 200 Å between the Fe atoms in our samples. To determine an absolute value for the Curie constant we calibrated our susceptometer with a superconducting sample. The values for the

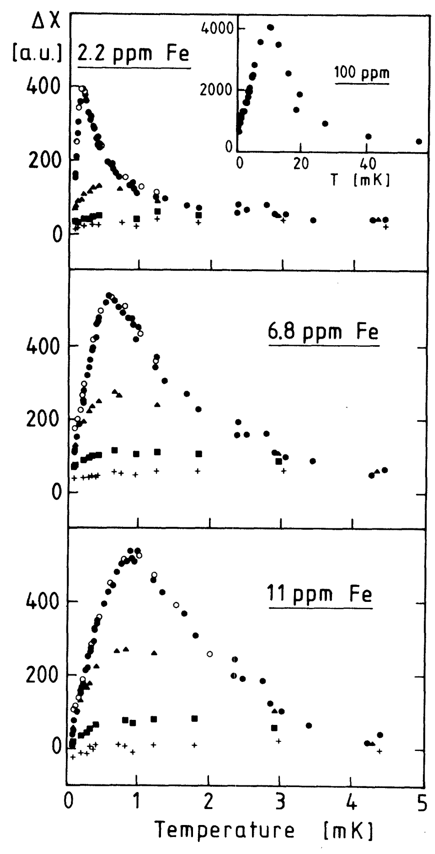

FIG. 1. Temperature dependence of the ac susceptibility of *Pd*-Fe samples measured at a frequency of 3 Hz and in fields of less than 1 mG (closed circles), of 0.76 G (triangles), 2.28 G (squares), and 3.8 G (plusses). The samples were cooled in a field of less than 1 mG. The open circles indicate data taken in less than 1 mG after the samples have been cooled from 1.2 K in a field of 3.8 G. The paramagnetic signal of pure Pd is less than 1% of the maximum signal of the dilute samples. A constant background has been subtracted.

effective magnetic moments (Table I) determined from the Curie constants, of course, bear the rather large uncertainty of this calibration, of the Curie plot, and of the determination of the Fe concentration (total about 30%).

In addition to the 3-Hz measurements we have performed measurements at 15 and 86 Hz. The maximum of the susceptibility occurred again at the same temperature within our uncertainty of 5%. This seems to be reasonable for a spin-glass because typical frequency dependences of T_f are between 1% and 30% per decade in frequency with a tendency to the lower value with decreasing concentration of the magnetic impurity,[9] which is below our detection limit.

As to the magnetic moment, the 15-Hz data agree with the 3-Hz data; the mean values for each sample from the 3- and 15-Hz data are given in Table I. They indicate that the moment is constant within the error. This shows that iron indeed is the dominant magnetic impurity. The measurements at 86 Hz clearly showed the influence of the smaller skin depth resulting in a smaller susceptibility signal.

According to our mass spectroscopic analysis, the concentrations of Cr, Mn, Co, and Ni are below 1 ppm in our samples. *Pd*-Co and *Pd*-Cr are Kondo systems at low temperatures,[10,11] and isolated Ni atoms show no moment in Pd.[12] Therefore, these impurities should not contribute to our data. Mn in Pd has a giant moment of $7.5\mu_B$[13]; as a consequence 1 ppm of Mn might give a noticeable contribution to the data of our most dilute sample. This contribution should be smaller in the higher concentration samples where we observed a moment which is even larger. It is therefore reasonable to assume that we see no influence of Mn as well.

Previous data of Webb, Crabtree, and Vuillemin,[3] measured on a 3.2 at. ppm *Pd*-Fe sample in 20 G, indicate a spin-glass transition at 7 mK. Their sample was a single crystal produced by zone refining in air and had a resistivity ratio $\rho(300\ \mathrm{K})/\rho(4.2\ \mathrm{K})$ of 15300. To investigate whether the sample preparation is decisive, we have annealed our samples for 7.5 h at 1100 °C in 1 bar of air. This resulted in an increase of the residual resistivity ratio and *reduced* the temperature of the susceptibility maximum slightly (see Table I and Fig. 2). To distinguish the possible influence of the air atmosphere from the influence of the larger mean free path of the conduction electrons in the air-annealed samples we have also rolled the 6.8- and 11-ppm samples to half their thickness. This reduced the residual resistivity ratio by about a factor of 6 but did not change the temperature of the maximum any further. This is not surprising because even at the low residual resistivity ratio of about 200, the mean free path of the conduction electrons is still about 1 μm and substantially larger than the mean separation of Fe atoms. It seems that a small part of the iron impurities has been rendered nonmagnetic by air annealing, a change into the wrong direction to explain the differences from Ref. 3.

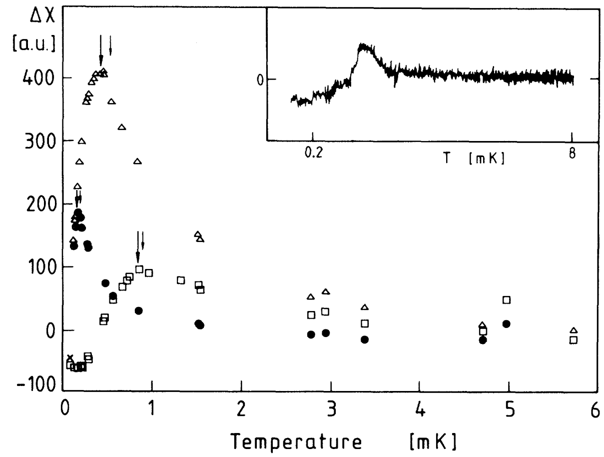

FIG. 2. Temperature dependence of the 3 Hz, zero-field susceptibility of the 2.2-ppm (circles) and of the 6.8-ppm samples (triangles) after annealing them in air and of the 11-ppm sample after annealing that sample also in air but then rolling it (squares). The negative susceptibility of this sample at very low temperatures increased slightly in a field of 3.8 G (cross). The inset shows the continuously recorded susceptibility of this sample obtained in a further run (the temperature scale is not linear here). The large arrows compare the freezing temperatures T_f from this experiment to T_f of the vacuum-annealed samples (small arrows) from Fig. 1. The data in the figure cannot be compared quantitatively to the data in Fig. 1 because of a change in the detection circuitry. A constant background has been subtracted.

Rolling substantially reduced the value of the susceptibility (see Fig. 2). In addition, the susceptibility below the maximum saturates and is smaller than the susceptibility background at high temperatures. This reduced susceptibility could be slightly increased by applying a field of several gauss. This observation needs further investigation.

We conclude from our investigation that *Pd*-Fe in the parts per million concentration range for Fe is a spin-glass at ultralow temperatures. The freezing temperature is proportional to the iron concentration, indicating that the interaction is proportional to (distance of the moments)$^{-3}$.

Former measurements of the polarization of the conduction electrons in 150-ppm *Pd*-Fe by positive muons have shown that the internal field produced by RKKY polarization is a factor of 5.5 larger than the local dipole field.[14] The occurrence of a RKKY spin-glass state in spite of the rather large mean distance between the Fe atoms demonstrates the very long range of the RKKY interaction when this interaction is not limited by a short mean free path of conduction electrons.

Our measurements show that far away from ferromagnetism and from the conventional spin-glass regime (our values of x, T, and B are almost 3 orders of magnitude smaller than in conventional spin-glass measurements) the common phenomenological concept of spin-glasses is still kept intact.

By studying the effect of air annealing on the freezing temperature we found a small reduction of active magnetic moments which is thought to be responsible for the increase of the residual resistivity ratio. The effect is surprisingly small and goes into the opposite direction as in the higher concentrated ferromagnetic range.[15] This difference is not understood; possibly Fe in Pd oxidizes in several steps with concentration-dependent products as it does in Cu.[16]

The observed effective moment of about $10\mu_B$ agrees with former measurements on more concentrated samples investigated at higher temperatures and higher fields (for example, Refs. 1, 4, and 7). This shows that the magnetic character of the iron atoms and the extension of the polarization clouds have not changed as one might expect at very low temperatures and very small concentrations.

Because of their spin-glass freezing, iron impurities should not be very effective spin scattering centers, and therefore not very detrimental to singlet superconductivity below the freezing temperature. We conclude that pure palladium should become neither superconducting nor magnetic above 79 μK.

We did not observe any evidence for magnetic ordering or spin freezing in our $Pt_{1-z}Ir_z$ samples with $0 \leqslant z \leqslant 0.8$ which contained between 10 and 40 at. ppm Fe (the samples with $z \geqslant 0.65$ showed superconductivity) at temperatures $T \geqslant 76$ μK.

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