Conduction-Electron Polarization in Dilute *Pd*Fe Alloys Studied by Positive Muons

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The μ^+ spin-rotation method was used to probe conduction-electron polarization in ferromagnetic *Pd*Fe (0.28 at.%) and spin-glass *Pd*Fe (0.015 at.%) from 0.11 to 300 K with reference to pure Pd. The result was explained in terms of the Ruderman-Kittel-Kasuya-Yosida spin oscillation in the region outside the giant moment.

Metallic Pd with dilute Fe impurities has interesting magnetic properties at low temperatures—the impurity Fe spin strongly polarizes the *d* holes on neighboring Pd sites, forming a large polarized complex (~ 10 Å) called the giant moment.[1,2] These giant moments couple to one another to yield long-range ferromagnetism at quite low Fe concentrations. For even lower concentrations, magnetic susceptibility measurements[3] show that these moments become antiferromagnetic, exhibiting spin-glass ordering below a critical concentration of 0.1 at.%. The origin of the spin-glass ordering might be the indirect coupling through the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction which, as predicted theoretically by Moriya,[4] becomes dominant outside the giant moments. In order to understand the mechanism, it is interesting to study the difference between the conduction-electron polarization above and below the critical concentration.

To this aim, polarized positive muons are used. Diffusion studies of hydrogen in Pd metal[5] indicate that the μ^+, after selecting a location randomly, will stay preferentially at octahedral interstitial sites and might be localized there at low temperatures. When the μ^+ stops in a metal with dilute magnetic impurities, it feels the contact fields from conduction electrons, that is, the contact field from polarized *d* holes or from *s* electrons which might be polarized through *s-d* hybridization. In addition to this, it feels dipolar fields. Both of these have field inhomogeneities. The fields and their inhomogeneities can be measured via the precession frequency and its dephasing time constant in the asymmetric positron decay of the μ^+.

The following samples were used in the present experiment: (1) Pure Pd wires with impurity concentration below 5 ppm, (2) Pd metal with 0.015-at.% Fe impurity, and (3) Pd metal with 0.28-at.% Fe impurity. The impurity concentrations in these samples have been confirmed by susceptibility measurements down to 1.25 K in comparison with the existing data.[3] According to the susceptibility data,[3] 0.015-at.% Fe becomes antiferromagnetic or spin-glass at around 0.4 K, while 0.28-at.% Fe becomes ferromagnetic at 9.0 K.

The polarized positive-muon beam at the Lawrence Berkeley Laboratory 184-in. cyclotron was used. The samples were cooled using a ^{3}He-^{4}He dilution refrigerator in an external field of 1.1 kG applied along the longest axis which is perpendicular to the μ^+-beam direction. The temperature was determined by a calibrated carbon resistor, Matsushita 68 Ω and $\frac{1}{8}$ W.[6] The details of the experimental technique and arrangement were almost the same as those of our previous low-temperature μ^+ spin-rotation experiment on Ni.[7] An additional experiment was carried out for pure Pd metal in 4.5 kG at room temperature in order to compare our data with the recent NMR result on hydrogen impurity in Pd metal.[8]

The observed time spectra of decay positrons for 0.28-at.% Fe are shown in Fig. 1. We can see a difference in the damping of the precession amplitude as the temperature changes through the transition temperature, which was also observed for 0.015-at.% Fe. In contrast, pure Pd did not show any significant change in the precession pattern and the relaxation-time constants were always longer than 20 μsec. These time spectra yielded a local magnetic field $[B_\mu \equiv f(\mathrm{kHz})/13.554$ G$]$ at the interstitial μ^+ and a field inhomogeneity (ΔH). The results of the analysis are summarized in Table I. They are expressed as a percentage of B_{ext} which was determined by the precession frequency in a Cu target using the known correction for the Knight shift of the μ^+ in Cu.[9]

The local field, B_μ, can be decomposed as follows:

$$B_\mu = B_{\mathrm{ext}} + (\tfrac{4}{3}\pi - D)M + H_{\mathrm{int}}, \tag{1}$$

where the second term is the correction due to the Lorentz field and demagnetizing field and H_{int} is the contact hyperfine field due to conduction-electron polarization. For pure Pd, the dipolar

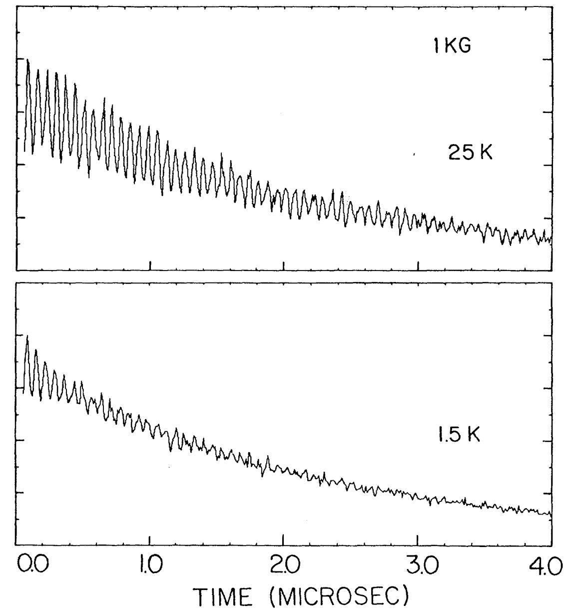

FIG. 1. Time spectrum of decay positrons from positive muons in *Pd*Fe (0.28-at.% Fe) at 25 and 1.5 K.

fields from the neighboring atoms inside the Lorentz cavity are canceled because of the cubic symmetry of the μ^+ location, while for *Pd*Fe alloys those from the giant moments inside the cavity are also canceled because of the random distribution of Fe impurities.[10] In Table I, we show $\frac{4}{3}\pi M$ estimated by interpolating the susceptibility data,[3] and the resultant H_{int}. In addition, we defined the ratio (reduced hyperfine field), $X = H_{\text{int}}/(\frac{4}{3}\pi M)$ which will be a convenient measure of the conduction-electron polarization normalized by the bulk magnetization. At low temperatures, $X = -0.54 \pm 0.14$ for 0.015-at.% Fe at 0.11 K and $X = -0.89 \pm 0.06$ for 0.28-at.% Fe at 1.5 K, while $X = -2.0 \pm 0.6$ for pure Pd at room temperature. The latter value is consistent with the precise NMR measurements on hydrogen in pure Pd.[8]

A recent polarized-neutron experiment on pure Pd revealed a rather large positive spin density at the octahedral site together with a slightly negative background.[11] This seems to contradict the fact that the observed H_{int} is negative. The situation is totally different from the case of Ni where the negative μ^+ hyperfine field was directly related to a negative spin density observed by the neutron experiment.[12] Detailed theoretical study is definitely required.

The extracted values of the field inhomogeneity ΔH are shown in the last column of Table I. In Fig. 2, we show the temperature dependence of H_{int} and ΔH for these two *Pd*Fe alloys. At the lowest temperature which is well below the ordering temperature, ΔH is almost 3 times larger than H_{int} for 0.28-at.% Fe while ΔH is 18 times larger than H_{int} for 0.015 at.%. By normalizing ΔH to $\frac{4}{3}\pi M$, we obtain $\Delta X = 10 \pm 1$ for 0.015-at.% Fe while it is 2.7 ± 1.0 for 0.28-at.% Fe. In addition, within a limited number of our data, the following point seems to be clear: Contrary to the sharp change in ΔH and H_{int} at around T_c for 0.28-

TABLE I. Summary of μ^+ spin rotation in Pd and *Pd*Fe.

Sample	T (K)	B_{ext}	$\frac{(B_\mu - B_{\text{ext}})}{B_{\text{ext}}}$ (%)	$\frac{4\pi M/3}{B_{\text{ext}}}$	$\frac{H_{\text{int}}}{B_{\text{ext}}}$ [a] (%)	$\frac{H_{\text{int}}}{4\pi M/3}$ (≡X)	$\frac{\Delta H}{B_{\text{ext}}}$ (%)
Pure Pd	300	4471.7(4)	- .028(12)	.027	- .055(15)	-2.0(6)	small
	4.2	1095.5(3)	+ .03 (4)	.036	- .01 (4)	- 0 (1)	small
	0.13	1095.5(3)	+ .09 (9)	.036	+ .06 (9)	+ 2 (3)	small
*Pd*Fe 0.015 at .% Fe	77	1081.0(3)	- .00 (3)	.035	- .03 (3)	- .8(8)	.3 (1)
	4.2	1081.0(3)	- .01 (3)	.058	- .05 (3)	- .9(5)	1.3 (3)
	0.6	1081.0(3)	+ .03 (3)	.18	- .11 (4)	- .6(2)	2.2 (3)
	0.11	1081.0(3)	+ .08 (4)	.37	- .20 (5)	- .54(14)	3.5 (2)
*Pd*Fe 0.28 at .% Fe	77	1074.8(4)	+ .05 (5)	.082	- .02 (5)	- .2 (6)	.42(5)
	25	1074.8(4)	+ .01 (3)	.26	- .2 (3)	- .8 (12)	1.5 (1)
	4.2	1092.2(2)	- .2 (3)	6.9	-5.9 (3)	- .86(4)	15 (4)
	1.5	1074.8(4)	- .5 (4)	7.0	-6.2 (4)	- .89(6)	19 (7)

[a] We have taken $D = 0$ for pure Pd, $D = 1.1 \pm 0.4$ for 0.015 at.% Fe, and $D = 0.8 \pm 0.2$ for 0.28 at.% Fe.

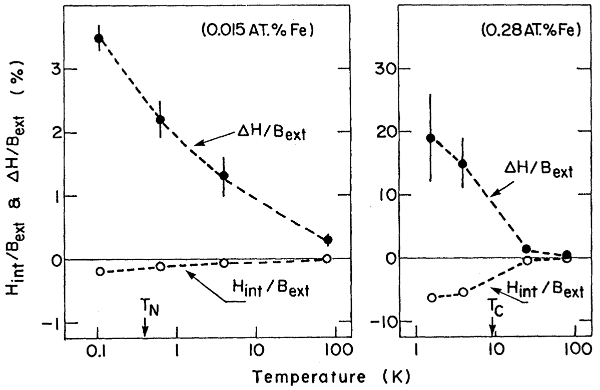

FIG. 2. Temperature dependence of the μ^+ hyperfine field (H_{int}) and the field inhomogeneity at μ^+ site (ΔH) for 0.015 at.% Fe and 0.28 at.% Fe, both of which are normalized by the applied field (B_{ext}). The temperature T_N corresponds to an antiferromagnetic or spin-glass transition temperature for 0.015 at.% Fe and T_C corresponds to a ferromagnetic transition temperature for 0.28 at.% Fe, both of which are estimated from the susceptibility data (Ref. 3).

at.% Fe, there is only a gradual change through T_N for 0.015-at.% Fe. As indicated by the susceptibility data,[3] this might be due to the applied field of 1 kG which smeared out the sharp transition as in the similar cases of *Cu*Mn and *Au*Fe.[13] The giant moments in 0.015-at.% Fe are aligned almost completely along the 1 kG field at 0.1 K.

Herein we offer some explanations for our experimental results for *Pd*Fe alloys. In the case of 0.015-at.% Fe, the average distance between the giant moments is around 40 Å. If we assume the size of the giant moment in such a low-Fe-concentration alloy is the same (~10 Å) as for higher concentrations, the distance is much larger than the size of the giant moment. Therefore, most of the μ^+ stay in the region outside the giant moment. On the other hand, since the susceptibility of *Pd*Fe alloys increases linearly with the Fe concentration only up to 0.3-at.% Fe, the giant moments are just starting to overlap with each other at 0.28-at.% Fe, so that the contact fields on the μ^+ originate from the polarized d holes inside the giant moment which is formed by the exchange-enhancement effect in the d band. Superimposed on this and dominant in the region outside the giant moments, we expect a conduction-electron polarization from the RKKY exchange interaction with the Fe moment without enhancement effect.[4] The conduction-electron polarization changes rapidly with position. This spin oscillation is thus responsible for the large inhomogeneity (ΔX) for 0.015-at.% Fe but it does not contribute to a net line shift, resulting in almost the same values of χ for those two *Pd*Fe alloys. This spin oscillation is related to the mechanism which produces spin-glass ordering of the giant moments in the *Pd*Fe alloy with Fe concentrations below 0.1 at.%.

The magnitude of the observed field inhomogeneity can be explained qualitatively using a theory which was intended for the case of great dilution. The main sources of the broadening are the dipolar field from the randomly located giant moments (ΔH_d) and the broadening due to the RKKY fields from randomly distributed Fe impurities (ΔH_{RKKY}). The contribution of ΔH_{RKKY} can be estimated from the theory of Walstedt and Walker,[10] based on the following assumptions: (1) The hyperfine coupling constant between conduction d electron and the μ^+ which appears in the RKKY amplitude can be replaced by the observed H_{int} for pure Pd at room temperature, corrected for the change of susceptibility; and (2) we take J (exchange coupling strength) to be 0.15 eV,[14] n/N (number of d holes per Pd atom) to be 0.36,[15] $2k_F$ to be 1.25 Å^{-1},[4] and S (Fe spin) to be 3.5.[16] We obtained $\Delta H_d = 73$ G and $\Delta H_{RKKY} = 371 \pm 97$ for 0.28-at.% Fe. The sum of these gives much larger value than the ΔH of 200 ± 75 obtained for 0.28-at.% Fe at the lowest temperature. This is probably due to an overestimate of ΔH_{RKKY}, which should be suppressed by the neighboring Fe impurities. However for 0.015-at.% Fe, we obtained $\Delta H_d = 3.6$ and $\Delta H_{RKKY} = 20 \pm 5$. The sum of these comes close to the observed value of 38 ± 2 at the lowest temperature.

The static shifts, X, for *Pd*Fe alloys are only about half of those for the pure Pd. If we renormalize X with respect to the induced Pd moments along ($6.5\mu_B$ out of $10\mu_B$), neglecting the contribution to M from the Fe moments at the centers of the giant moments, we find almost the same contact field per average Pd moment in all three cases (within 40%), suggesting that the conduction-electron polarization simply depends on the polarization of Pd atoms regardless whether the latter is formed by an external field or by the Fe impurities.

Recently Nieuwenhuys[17] proposed a picture, based on the specific heat data, of giant moments with a distribution of effective g values in Pd atoms arising from the fluctuations in the polarized Pd cloud; if so, the μ^+ might be depolarized dynamically as a result of magnetic coupling with such fluctuations. Detailed analysis including an explanation of the enhancement in the ratio $\Delta H/$

$H_{\rm int}$ in paramagnetic phase will be required.

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