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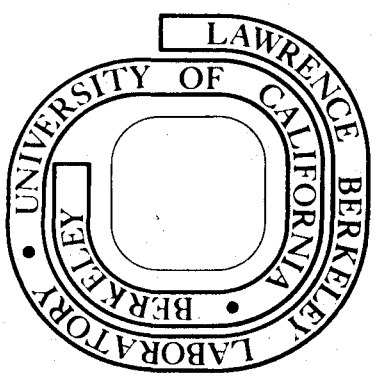

DISCLAIMER

Conduction Electron Polarization in Very Dilute PdFe Alloys Studied by Positive Muons

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In order to investigate the ordering mechanism among the giant moments around Fe in Pd, the μ^+ was used to probe conduction electron polarization in ferromagnetic PdFe (0.28 at .%) and spin-glass PdFe (0.015 at .%) from 0.11 K to 300 K with reference to pure Pd. Below the ordering temperature the observed shifts, when normalized by the bulk magnetization, are almost the same. However, the normalized broadening for the spin-glass alloy is substantially larger than for the ferromagnetic alloy. Using the observed shift for pure Pd, the result was explained in terms of the RKKY 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 neighbouring Pd sites, forming a large polarized complex called the giant moment. Of the total moment of approximately 10 μ_B [1], only one third resides on the Fe impurity, while the rest is distributed over an extended polarization cloud ($\sim$ 10 A) surrounding the Fe impurity [2]. These giant moments couple to one another to yield long-range ferromagnetism at very low Fe concentration. For even lower concentration, magnetic susceptibility measurements [3] show that these moments become anti-ferromagnetic exhibiting spin glass ordering below a critical concentration of 0.1 at .% corresponding to an average distance between impurity atoms of 15 to 20 A. The origin of the spin glass ordering might be the indirect coupling through the RKKY interaction which, as predicted theoretically by Moriya [4], becomes dominant outside the giant moments. In order to understand the details of the mechanism, it is quite interesting to study the difference between the conduction electron polarization above and below the critical concentration.

Polarized positive muons are used here to probe the conduction electron polarization in PdFe alloys. The 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 due to the random distribution of the field sources. The fields

and their inhomogeneities can be measured via the precession frequency and its dephasing time-constant in the asymmetric position decay of the μ^+. In the present experiment, we have found evidence of the RKKY oscillation in the region outside the giant moment.

The following samples were used in the present experiment: (1) pure Pd wires with impurity concentration below 5 ppm (1 mm diameter and 50 mm long wires, loosely banded into a 40 mm x 50 mm x 8 mm rectangular shape), (2) Pd metal with 0.015 at .% Fe impurity (45 mm x 32 mm x 8 mm rectangular shape), and (3) Pd metal with 0.28 at .% Fe impurity (65 mm x 35 mm x 8 mm approximately ellipsoidal shape). 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 anti-ferromagnetic 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 inch 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 resister, Matsushita 68 Ω 1/8 watt[6]. The details of the experimental technique and arrangement were almost the same as those of our previous low temperature μ^+SR 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 0.015 at .% Fe at 4.2 K and 0.11 K and for 0.28 at .% Fe at 25 K and 1.5 K are shown in

Fig. 1 (a) and 1 (b), respectively. We can see a difference in the damping of the precession amplitude as the temperature changes through the transition temperature. 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, indicating that the observed damping comes from the magnetization induced by Fe impurities. After subtracting the contributions from cryostat constituents, these time spectra were fitted to the following formula:

$$N(t) = N_0 \exp(-t/\tau_\mu)[1 + A\, G(t) \cos(2\pi ft + \phi)] \qquad (1)$$

where τ_μ is the muon mean life, A is the asymmetry, G(t) is an attenuation factor and f is the precession frequency, which yields a local magnetic field ($B_\mu \equiv f(kHz)/13.554$ Gauss) at the interstitial μ^+. The function G(t) describes the relaxation of muon polarization which, in our case, comes mainly from the static inhomogeneity of the local field. For the form G(t), we assumed both a Gaussian form ($G(t) = \exp(-\sigma^2 t^2)$) and an exponential form ($G(t) = \exp(-t/T_2)$). Although we found in some cases that a Gaussian form gave a better fit, the difference was not statistically significant and both gave the same field inhomogeneity (ΔH). The results of the analysis are summarized in Table 1. 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:

$$B_\mu = B_{ext} + (\frac{4\pi}{3} - D)M + H_{int} \qquad (2)$$

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 fields from the neighbouring atoms inside the Lorentz cavity are cancelled because of the cubic symmetry of the μ^+ location, while for PdFe alloys those from the giant moments inside the cavity are also cancelled because of the random distribution of Fe impurities[10]. In Table 1, we show $\frac{4\pi}{3}M$ estimated by interpolating the susceptibility data[3], and the resultant H_{int}, both of them being expressed as a percentage of B_{ext}. In addition, we defined the ratio (reduced hyperfine field),

$$X = H_{int}/(4\pi M/3) \qquad (3)$$

which will be a convenient measure of the conduction electron polarization normalized by the bulk magnetization. At low temperatures, X = -.54 (14) for 0.15 at .% Fe at 0.11 K and X = -.89 (6) for 0.28 at .% Fe at 1.5 K, while X = -2.0 (6) for pure Pd at room temperature. The extracted values of the field inhomogeneity (ΔH) are shown in the last column of Table 1. In Fig. 2, we show the temperature dependence of H_{int} and ΔH for these two PdFe alloys. As the temperature decreases ΔH increases in the same manner as H_{int} in both samples. However, at the lowest temperature which is well below the ordering temperature, ΔH is almost three 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 $\frac{4\pi}{3}M$, we obtain ΔX = 10(1) for 0.015 at .% Fe while it is 2.7(10) for 0.28 at .% Fe. In addition, contrary to the sharp change in ΔH and H_{int} at around T_c for 0.28 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 similarly to the cases of CuMn and AuFe[11]. The giant moments in 0.015 at .% Fe are aligned almost completely along the 1 kG field at 0.1 K.

For pure Pd, the resultant shift in H_{int} is obtained as -0.055 (15)%. The precise NMR measurements on hydrogen in pure Pd[6] showed a proton Knight shift of -0.012 (1)% at 343 K for the dilute limit of the hydrogen concentration which corresponds to the shift in H_{int} of -0.035 (1)% after the Lorentz field correction. The agreement is good after taking into account the change of the susceptibility from 0.066% to 0.056% as the temperature goes from 300 K to 343 K. It is interesting to compare this result with the spin density known from the neutron scattering experiment. A recent experiment on pure Pd revealed a rather large positive spin density at the octahedral site together with a slightly negative background[12]. 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[13]. Detailed theoretical study as well as examination of the neutron data is definitely required.

Now let us try to explain our experimental result for PdFe alloys. In the case of 0.015 at .% Fe the average distance between the gian moments is around 50 A, which is much larger than the size of the giant moment so that most of the μ^+ stay in the off-cluster region. On the other hand, as the susceptibility of PdFe 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 d-band[4,14]. Superimposed on this, we expect an RKKY spin oscillation caused by the exchange interaction between the localized Fe moment and the conduction electrons without enhancement effect[4]. This conduction electron polarization changes more rapidly with position and should become dominant in the off-cluster region[4]. The RKKY spin oscillation is thus responsible for the large inhomogeneity (ΔX) in the field for 0.015 at .% Fe while it does not contribute to a net line shift resulting in almost the same values of X for these two PdFe alloys. This spin oscillation is related to the mechanism which produces spin glass ordering of the giant moments in the PdFe alloy with Fe concentration below 0.1 at .%.

The magnitude of the observed field inhomogeneity can be explained using the theories which are adequate to the case of great dilution. The main source of the broadening for 0.28 at .% Fe is the dipolar field from the randomly located giant moments. The statistical theory[10,15] predicts that $\Delta H = 4.8 \times (\frac{4\pi}{3} - D)M$ which is almost the same value as what we obtained for 0.28 at .% Fe, that is $3.3(12) \times (\frac{4\pi}{3} - D)M$. But for 0.015 at .% Fe at the lowest temperature, this term should be around 13 G which is much smaller than the observed value of 38 (2)G. The broadening due to the RKKY fields from randomly distributed Fe impurities can be estimated from the theory of Walstedt and Walker[10]. The RKKY broadening in a fcc lattice is

$$\Delta H = \frac{16\pi}{3} \frac{Ac}{a^3} \qquad (4)$$

where c is the atomic fraction of impurities and a is the lattice constant. The parameter A is the RKKY amplitude coefficient which can be expressed in our case as,

$$A = 4\pi \frac{J}{\mu_B} |\langle S_z \rangle| \left(\frac{3n}{N}\right) \left(\frac{H_{int}}{B_{ext}}\right)_{Pd} \frac{1}{(2k_F)^3} \qquad (5)$$

where S is the localized Fe spin and J is the exchange coupling strength between d-holes and impurity Fe. The n/N means the number of d-holes per Pd atom. The hyperfine coupling constant between a conduction electron and the μ^+ has been replaced by the observed shift of the μ^+ hyperfine field for pure Pd at room temperature, corrected for the change of susceptibility. By taking J = 0.15 eV[16], n/N - 0.36[17], $2k_F$ = 1.25 A^{-1}[4], and $|\langle S_z \rangle|$ = 3.76[18] we obtain ΔH = 21 (6) G which accounts for the discrepancy between the dipolar broadening and the observed anomalous broadening in 0.015 at .% Fe.

The static shifts, X, for PdFe alloys are only about half of those for the pure Pd. If we renormalize X with respect to the induced Pd moments alone (6.5 μ_B out of 10 μ_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 no matter whether the latter is formed by an external field or by the Fe impurities. This picture is consistent with the interpretations of Pd NMR experiments[19] and polarized neutron scattering[12,20] for higher Fe concentration. Extension of the present work to higher concentration as well as a theoretical investigation of the

origin of the shift in pure Pd is highly recommended.

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Table 1 Summary of μ^+SR in Pd, PdFe

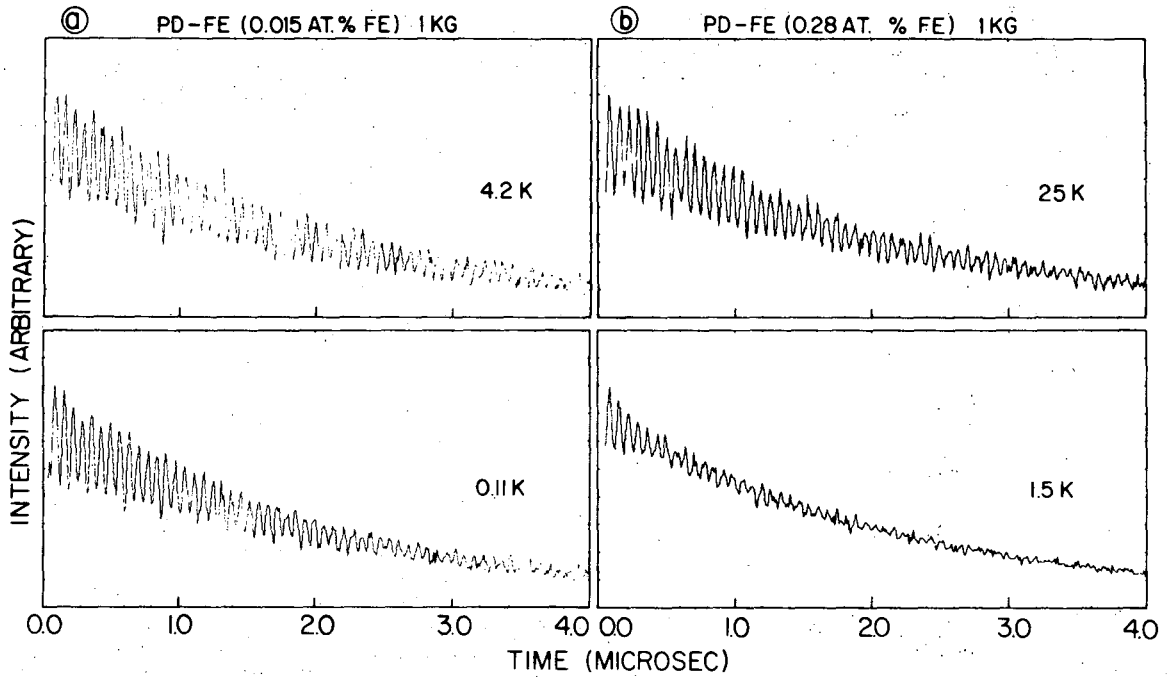
Sample	T (K)	B_{ext}	$\frac{(B_\mu - B_{ext})}{B_{ext}}$ (%)	$\frac{4\pi M/3}{B_{ext}}$	$\frac{H_{int}}{B_{ext}}$ *) (%)	$\frac{H_{int}}{4\pi M/3}(\equiv X)$	$\frac{\Delta H}{B_{ext}}$ (%)
Pure Pd	300	4471.7(4)	- .028(12)	.027	- .055(15)	-2.0(6)	small
	4.2	1095.5(3)	+ .03 (4)	.036	- .01 (4)	- 0 (1)	small
	0.13	1095.5(3)	+ .09 (9)	.036	+ .06 (9)	+ 2 (3)	small
PdFe	77	1081.0(3)	- .00 (3)	.035	- .03 (3)	- .8(8)	.3 (1)
0.015 at .% Fe	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)
PdFe	77	1074.8(4)	+ .05 (5)	.082	- .02 (5)	- .2 (6)	.42(5)
0.28 at .% Fe	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)

*) We have taken D = 0 for pure Pd, D = 1.1 (4) for 0.015 at .% Fe and D = 0.8 (2) for 0.28 at .% Fe

Figure Captions

Figure 1. Time spectrum of decay positrons from positive muons in PdFe (0.015 at .% Fe) at 4.2 K and 0.11 K (a), and PdFe (0.28 at .% Fe) at 25 K and 1.5 K (b).

Figure 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[3].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ⓑ PD-FE (0.28 AT. % FE) 1KG
4.2 K
25 K
0.11 K
1.5 K
INTENSITY (ARBITRARY)
0.0
1.0
2.0
3.0
4.0
TIME (MICROSEC)

Fig. 1

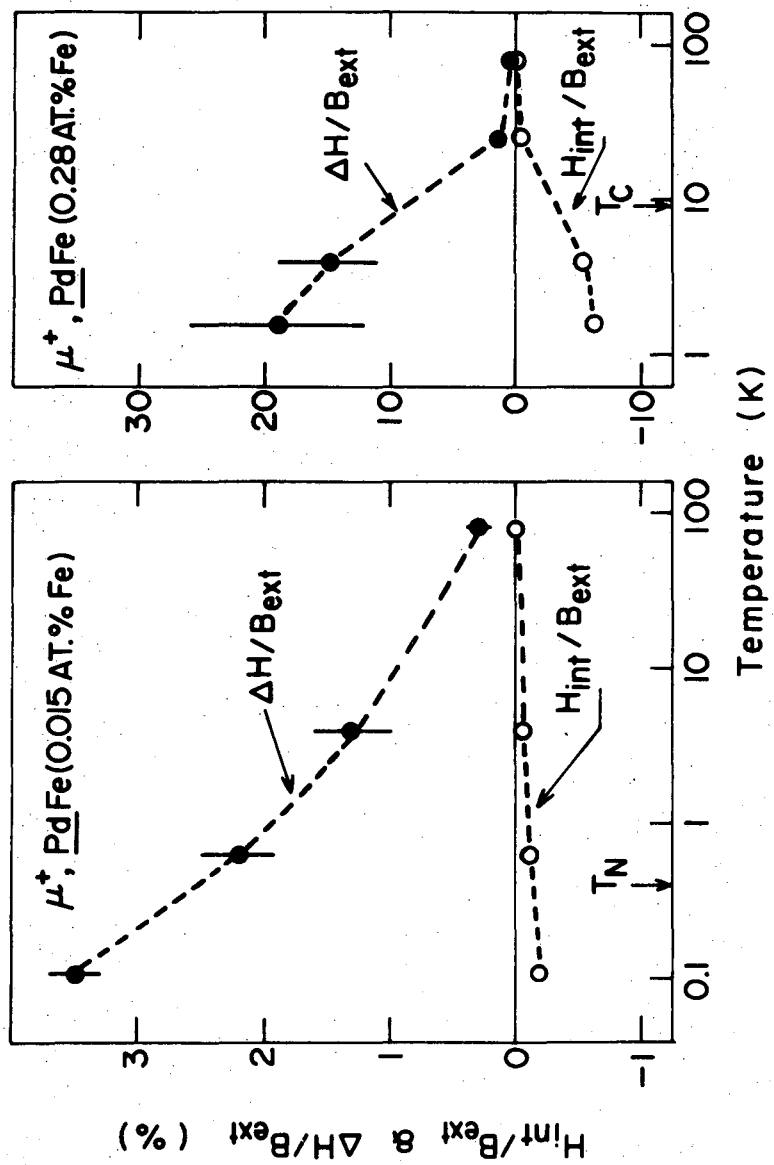

Fig. 2

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