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STUDIES OF DILUTE PdFe ALLOYS

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ABSTRACT

In order to investigate the ordering mechanism among giant moments around Fe impurities in Pd, μ^+ was used to probe the conduction electron polarization in PdFe alloys above and below the critical concentration of 0.1 at. % (i.e. 0.28 at. % Fe and 0.015 at. % Fe) with reference to pure Pd. Below the ordering temperatures (9.0 K and 0.4 K, respectively), the broadening of the μ^+ field for 0.015 at. % Fe is substantially larger than that for 0.28 at. % Fe, when normalized to the bulk magnetization. The results can be explained in terms of an RKKY spin oscillation in the region outside the giant moment.

1. INTRODUCTION

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 (~ 10 A) 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 measurements³ show a marked deviation from the Curie-Weiss law indicating a spin-glass ordering below a critical concentration of 0.1 at. % which corresponds to an average distance between impurity atoms of 15 to 20 A. However, a recent paper has proposed a different model; namely, a ferromagnetic ordering with a distribution of effective g-values in Pd atoms.⁴ In order to gather further insight into this problem, 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. When the μ^+ stops at a random site in a metal with dilute magnetic impurities, it feels contact fields from the 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, the μ^+ interacts with dipolar fields from the giant moments. Both of these have inhomogeneities due to the random distribution of the field sources. Such magnetic fields and their inhomogeneities can be measured via the precession frequency and its dephasing time-constant in the asymmetric positron decay of the μ^+ (μ^+ SR method).

As a reference for the PdFe studies, a separate μ^+ SR experiment was carried out to measure the μ^+ Knight shift in pure Pd. In the next section, the result obtained is compared with the relevant data on hydrogen in Pd. The properties of the μ^+ as a probe to study magnetic properties of Pd-based alloys is discussed. The experimental results on PdFe alloys are presented in Section 3 and their interpretations are given in Section 4.

2. THE μ^+ KNIGHT SHIFT IN Pd

Using known experimental data on the properties of hydrogen in Pd, we can make reasonable predictions for the properties of the μ^+ in Pd: these diffusion studies as well as neutron experiments⁵ indicate that the μ^+ will preferentially remain at octahedral sites and might be localized there for its entire lifetime (2.2 μ sec) below room temperature. Recently NMR experiments have been carried out to measure the proton Knight shift in Pd in the dilute limit,⁶ which could be compared to the μ^+ Knight shift observed at 300 K.

The μ^+ Knight shift experiment on pure Pd was recently carried out on the M9 channel of TRIUMF. A highly polarized μ^+ ($\sim 90\%$) beam was stopped in the Pd metallic target (1 mm diam and 50 mm long wires, loosely banded into a rectangular shape). Stability of the external field appropriate to the high precision of μ SR was achieved with a Varian Fieldial Mark II. The value of the external field was monitored frequently by replacing the Pd target with a Cu target and using the known correction for the Knight shift of μ^+ in Cu (+0.0081%).

The observed local field at the μ^+ site (B_{μ}) can be decomposed into a sum of the external field (B_{ext}), the Lorentz field ($4\pi/3 M$) and the contact field from polarized conduction electrons (Hint). We have neglected the demagnetizing field because of sample geometry. The dipolar fields from neighbouring atoms are cancelled

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because of the cubic symmetry of the μ^+ location which, as mentioned above, is expected to be localized at octahedral sites according to hydrogen data. The observed shift, $(B_{\mu}/B_{\text{ext}} - 1)$, was -0.013 (2) %. The resultant H_{int} is obtained as -0.040 (2) %. The NMR measurements on hydrogen in pure Pd have shown a proton Knight shift of -0.012 (1) % at 343 K for the dilute limit of hydrogen concentration,⁶ which corresponds to H_{int} of -0.035 (1) % after the Lorentz field correction. We can say that there is a good agreement between the hydrogen and μ^+ data, which suggests that the local magnetic structure as seen by the interstitial probes is rather independent of the mass of the probe. This result also seems to support our assumptions concerning μ^+ diffusion in Pd.

We have also measured the temperature dependences of the μ^+ Knight shift and the relaxation time in pure Pd down to 0.13 K.⁹ Although the statistics were poor, the Knight shift was found to be constant within 0.1% and the relaxation time was always longer than 20 μsec .

A recent polarized neutron experiment on pure Pd⁹ revealed a rather large positive spin density at the octahedral site, together with a slightly negative background between octahedral sites and Pd sites. This seems to contradict the above fact that the observed H_{int} is negative. It is also interesting to point out the difference between H_{int} in Pd and that in Ni. After normalizing to the magnetization, the effective hyperfine field X ($= 3H_{\text{int}}/4\pi M$) becomes -1.4 (1) for Pd while it is -0.31 for Ni. The Ni results appear consistent with neutron data.¹⁰ These facts indicate that the μ^+ field is mainly determined by the spin-dependent screening mechanism of polarized conduction electrons, which is quite different for Pd and Ni.

3. EXPERIMENTAL RESULTS ON PdFe ALLOYS⁸

The polarized positive muon beam at the Lawrence Berkeley Laboratory 184-inch cyclotron was used for these experiments. The samples were cooled using a $^3\text{He} - ^4\text{He}$ dilution refrigerator in an external field of 1.1 kg applied along the longest axis, which is perpendicular to the μ^+ beam direction. The details of the experimental technique and arrangement were almost the same as in our previous experiments on Ni.¹¹ The samples used in this experiment were (1) Pd metal with 0.015 at. % Fe impurity (45 mm x 32 mm x 8 mm rectangular shape), and (2) 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, though this interpretation has been questioned,⁴ while 0.28 at. % Fe becomes ferromagnetic at 9.0 K.

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. One can see a difference in the damping of the precession amplitude as the temperature changes through the transition temperature, in contrast to the temperature-independent relaxation in pure Pd, thus indicating that the observed damping comes from the magnetization induced by Fe impurities. These time spectra yield a local magnetic field ($B_{\mu} = f(\text{kHz})/13.554$ G) at the interstitial μ^+ and a field inhomogeneity (ΔH). The results of the analysis are summarized in Table I.

Following the same procedure as in pure Pd, the H_{int} was extracted, where the dipolar fields from giant moments inside the Lorentz cavity are taken as averaged to zero because of the random distribution of Fe impurities.¹² In Fig. 2, the temperature dependence of H_{int} and ΔH for these two PdFe alloys is shown. 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 H_{int} and ΔH to $4\pi M/3$, we obtain $X = -0.54$ (14) and $\Delta X = 10$ (1) for 0.015 at. % Fe while they are -0.89 (6) and 2.7 (10) for 0.28 at. % Fe. In addition, contrary to the sharp change in ΔH

Table I. Summary of $\mu^+\text{SR}$ in PdFe alloys

Sample	T (K)	$(B_{\mu} - B_{\text{ext}})$		$4\pi M/3$		$H_{\text{int}}^{\#}$		$H_{\text{int}}/4 M/3 (=X)$		ΔH Bext (%)
		Bext (%)	(%)	Bext (%)	(%)	Bext (%)	(%)	Bext (%)	(%)	
PdFe	77	-0.00	(3)	0.035	-0.03	(3)	-0.8	(8)	0.3	(1)
0.015	4.2	-0.01	(3)	0.058	-0.05	(3)	-0.9	(5)	1.3	(3)
at. % Fe	0.6	+0.03	(3)	0.18	-0.11	(4)	-0.6	(2)	2.2	(3)
	0.11	+0.08	(4)	0.37	-0.20	(5)	-0.54	(14)	3.5	(2)
PdFe	77	+0.05	(5)	0.082	-0.02	(5)	-0.2	(6)	0.42	(5)
0.28	25	+0.01	(3)	0.26	-0.2	(3)	-0.8	(12)	1.5	(1)
at. % Fe	4.2	-0.2	(3)	6.9	-5.9	(3)	-0.86	(4)	15	(4)
	1.5	-0.5	(4)	7.0	-6.2	(4)	-0.89	(6)	19	(7)

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

and H_{int} at around T_c for 0.28 at. % Fe, there is only a gradual change through the supposed 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. This is similar to the cases of CuMn and AuFe.¹³ As clearly shown in the knee of the magnetization curve, the giant moments in 0.015 at. % Fe are aligned almost completely along the 1 kG field at 0.1 K.

4. DISCUSSION

Herein we offer some explanations for our experimental results for PdFe alloys. In the case of 0.015 at. % Fe the average distance between the giant moments is around 40-50 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, 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 the d-band.¹⁴ Superimposed on this and dominant at the region outside the giant moments, we expect a conduction electron polarization from the RKKY exchange interaction with the localized Fe moment without enhancement effect.¹⁴ The conduction electron polarization changes rapidly with position. This spin oscillation is thus responsible for the large inhomogeneity (ΔX) in the field for 0.015 at. % Fe but 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 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 source of the broadening for 0.28 at. % Fe is the dipolar field from the randomly located giant moments. The statistical theory¹² predicts almost close value to ΔH , obtained for 0.28 at. % Fe. But for 0.015 at. % Fe at the lowest temperature, this term will be one order of magnitude 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 Walsstedt and Walker.¹² The hyperfine coupling constant between conduction electrons and μ^+ which appears in the RKKY amplitude can be calculated from the observed H_{int} for pure Pd at room temperature, corrected for the change of susceptibility. By taking J (exchange coupling strength) = 0.15 eV,¹⁵ n/N (number of d-holes per Pd atom) = 0.36,¹⁶ $k_F = 1.25 \text{ \AA}^{-1}$,¹⁴ and

S (Fe spin) = 3.5,¹⁷ we obtain the value which partly 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 smaller than 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 centres of the giant moments, we find almost the same contact field per average Pd moment in all three cases (within 30%), suggesting that a part of the conduction electron polarization sensed by the μ^+ simply depends on the polarization of Pd atoms no matter whether the latter is formed by an external field or by the Fe impurities.

Based on the specific heat data, Nieuwenhuys⁴ proposed a picture of giant moments with a distribution of effective g -values in Pd atoms arising dynamically. In this picture the polarized Pd cloud couples to the local moment on the Fe atom with a characteristic time-constant. The μ^+ may have a possibility to probe the polarization cloud and solute Fe differently.¹⁸ We note that the μ^+ senses a time-period of dynamical behaviour which is somewhat between the range for neutrons and susceptibility measurements. Detailed analysis is required.

5. SUMMARY

Dilute PdFe alloys above and below the critical concentration of 0.1 at. % have been studied by the μ^+ SR method. Below the ordering temperature the observed shifts, when normalized to the bulk magnetization, are almost the same. However, the normalized broadening for the spin-glass alloy is substantially larger than for the ferromagnetic alloy. To date, two experimental results have indicated a possible spin-glass ordering below the critical concentration: 1) the magnetic susceptibility deviates from the Curie-Weiss law,³ 2) below the ordering temperature, the specific heat does not depend very much on the concentration.¹⁷ We think the μ^+ results are further support of spin-glass ordering below the critical concentration.

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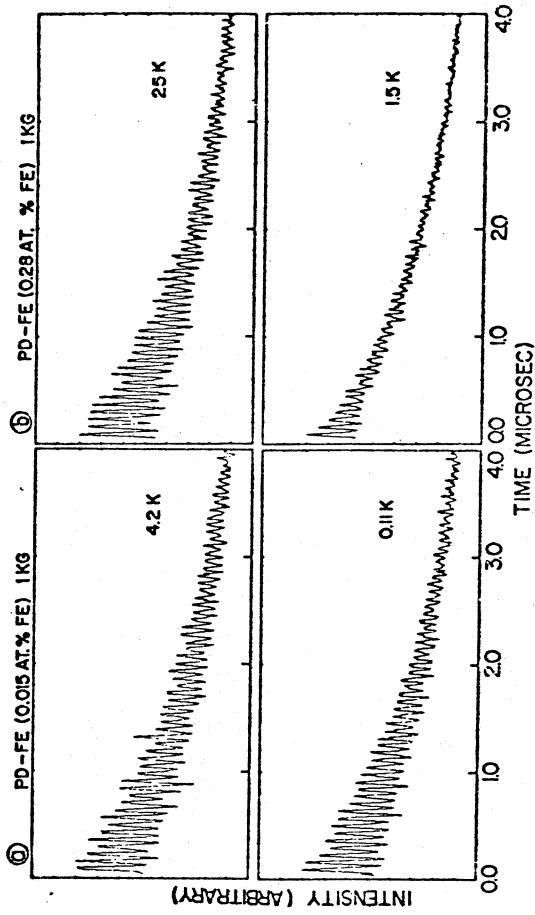


Fig. 1. Time spectrum of decay positrons from positive muons in $\underline{\text{PdFe}}$ (0.015 at. % Fe) at 4.2 K and 0.11 K (a), and $\underline{\text{PdFe}}$ (0.28 at. % Fe) at 25 K and 1.5 K (b).

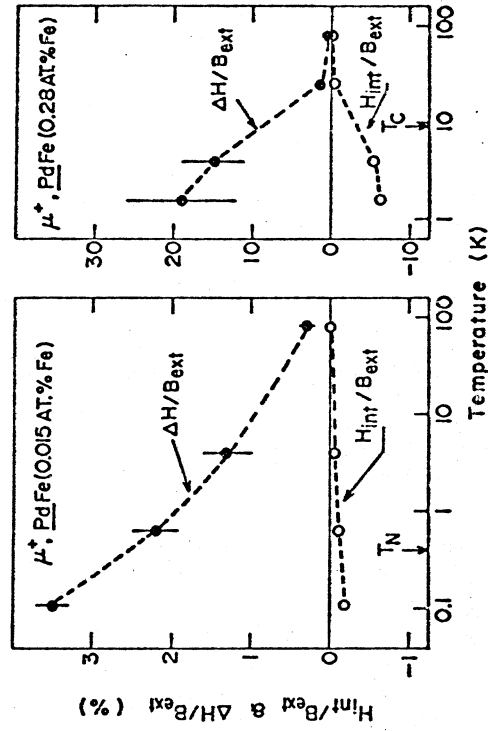


Fig. 2. Temperature dependence of the μ^+ hyperfine field (H_{int}) and the field homogeneity at the μ^+ site (ΔH) for 0.015 at. % Fe and 0.28 at. % Fe, both of which are normalized by the applied field (B_{ext}). The temperature T_N corresponds to an antiferromagnetic or spin-glass transition for 0.015 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