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# The search for magnetic order in $\delta$-Pu metal using muon spin relaxation

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**Abstract**

We review results from previous muon spin relaxation ($\mu$SR) measurements in applied fields of $H_0 = 0$ and 0.25 T which established an upper limit for the ordered or disordered frozen spin moment above $T = 4$ K in $\delta$-Pu (4.3 at. % Ga) of $\mu_{\rm ord} \leq 10^{-3}\mu_{\rm B}$. In addition, we present new data in $H_0 = 0.25$ T and 2 T applied field on a highly annealed $\delta$-Pu (4.3 at. % Ga) sample. Neither the muon Knight shift ($H_0 = 2$ T) nor the inhomogeneous linewidths in the new sample show appreciable temperature dependence below about T = 60 K, also consistent with no spin freezing. Recent theoretical arguments advanced to explain these results are mentioned.

*Key words:* actinide alloys and compounds, muon spectroscopies

## 1. Introduction

The question of whether there is magnetic order in most metals has long been settled. This is because the necessary measurement techniques (specific heat combined with neutron scattering, for example) are common, and so are the methods for readily producing high-quality materials. This has not been the case with Pu metal, however, the study of which has been hindered by difficulties in handling this toxic, radioactive material. Thus, materials containing the more stable actinide atoms have received greater attention. For example, interest in 5f-electron materials in general has been strong since the discovery of heavy fermion superconductivity in $UBe_{13}$[1] and $UPt_3$[2] decades ago. Interest in Pu compounds, however, has only recently taken root outside of the small 'Pu community' with the discovery of superconductivity in $PuMGa_5$, M = Co [3], Rh [4].

Meanwhile, a quiet debate about the nature of the $5f$ electrons in Pu metal has been brewing. Pu metal exists in six allotropic phases as a function of temperature and volume. In order to account for the larger volume of the $\delta$ phase of Pu, which has fcc structure and is stable near 700 K, theorists have found it necessary to localize a significant fraction of its five $5f$ electrons [5]. This is in contrast to the stable, lower-volume (-25%) room-temperature $\alpha$-phase of Pu, where the $f$-electrons are itinerant. The theoretical localization of $\delta$-Pu's $f$-electrons has led to numerous predictions of magnetic order [6]. This situation led Lashley *et al.* to publish a compendium of experimental results refuting magnetism in $\delta$-Pu,

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citing a limit for the ordered moment from neutron scattering of between 0.04 - 0.4 $\mu_B$ [7].

Against this background, we began a study of both $\alpha$-Pu and $\delta$-Pu(4.3 at. % Ga) in 2004 using the muon spin relaxation technique ($\mu$SR). $\mu$SR is particularly suitable for this task because of its high sensitivity to small-moment magnetism, wherein ordered moments as small as 0.001 $\mu_B$ can be detected. (In Kondo lattice systems, for example, small magnetic moments can survive at temperatures much less than the effective Kondo temperature.) Furthermore, because the muon is a local (interstitial) probe, the signal is a sum over points in momentum space, and, thus, $\mu$SR is equally sensitive to the ordered or *disordered* freezing of the spins.

## 2. Experimental setup and data analysis

We carried out two sets of measurements in $\delta$-Pu(4.3 at. % Ga). The sample for the first set of measurements in applied field $H_0 = 0$ and 0.25 T was approximately 12 mm in diameter and 0.1 mm thick, consisting of $^{239}$Pu(93.7%), with smaller concentrations of $^{240}$Pu(5.86%) and $^{238}$Pu(0.17%), and a dominant magnetic impurity content of Fe(235 at. ppm) [8]. This sample was annealed for approximately 43 hours at 440 C, and is referred to as $\delta$-Pu(a). The second $\delta$-Pu (4.3 at. % Ga) sample was isotopically identical to the first, with the same impurity concentration, but was annealed for approximately 200 hours at 465 C. This sample, denoted $\delta$-Pu(b), was used for high-field experiments ($H_0 = 2$ T) where muon Knight shift measurements could be performed. The susceptibility for these two samples is shown in Fig. 1, together with the susceptibility for our $\alpha$-Pu. Data taken on $\delta$-Pu(a) and $\alpha$-Pu have been published previously [8].

The experiments were performed at the M20 surface muon channel at TRIUMF in Vancouver, Canada. The samples were encapsulated inside a 70 $\mu$m thick Kapton coating and were placed inside a Ti cell under He atmosphere to prevent contamination. The cell possessed a thin 50 $\mu$m Ti window to allow the muon beam to enter. A negligible fraction of the beam stopped inside the Kapton or Ti window.

In a $\mu^+$SR experiment 100% polarized positive muons are implanted in a sample and come to rest at interstitial sites in the lattice. In our experiments the muon polarization was rotated approximately 90 deg vertically from the incoming muon momentum.

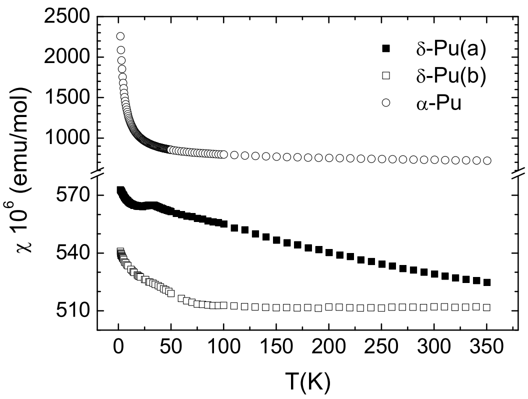


Fig. 1. Temperature dependence of the static susceptibility in 2T applied field for the two measured $\delta$-Pu samples: (a) annealed for 43 hours at 440 C and (b) annealed for 200 hours at 465 C. For comparison the susceptibility of $\alpha$-Pu is also shown.

The applied field was transverse to the muon spin (TF) and along the beam axis. The muon decays via the weak interaction into a detected positron and two undetected neutrinos with a half-life of 2.2 $\mu$s. The time evolution of the muon polarization is monitored by recording the time difference between the muon stop signal and the spatially anisotropic positron decay signal, resulting in a histogram of the muon polarization (or asymmetry) versus time [9]. In a TF experiment one measures the muon precession frequency $\nu$ and the damping rate of the precession signal $\sigma$, which is a measure of the inhomogeneous field distribution inside the sample.

The $\mu$SR data for these TF experiments were well described by the sum of two Gaussian-damped functions, one for Pu $[\exp(-\sigma^2 t^2/2)\cos(2\pi\nu + \phi)]$ and a similar one for Ti. The background signal from the Ti cell was characterized in separate experimental runs without the sample, and the damping rate from this source was held fixed at the measured values (as a function of temperature and field) in the fits to the Pu data [8].

## 3. Results and Discussion

The damping rates $\sigma$ for measurements in $H_0 = 0.25$ T in $\delta$-Pu(a) and $\delta$-Pu(b) are shown in Fig. 2. As described in Ref. [8], it was established that the muon relaxation was not affected by the buildup of damage caused by the radioactive decay of Pu. The rates in Fig. 2 are comparable to the rates found

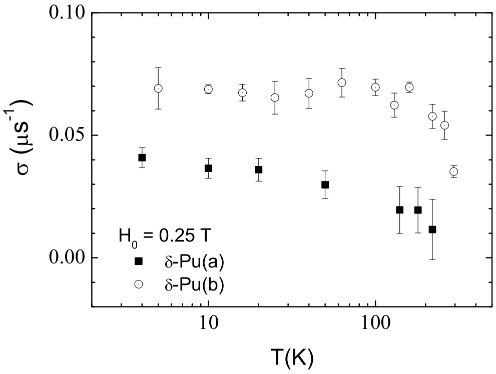


Fig. 2. Temperature dependence of the Gaussian damping rate $\sigma$ in $\delta$-Pu(a) and $\delta$-Pu(b) in $H_0 = 0.25$ T applied field. The small, relatively temperature-independent magnitude of $\sigma$ is consistent with no ordered or disordered $f$-electron spin freezing.

in zero applied field, where no coherent precession of the muon spin was observed. (Precession would be expected for magnetic order.) If disordered spin freezing occurred one would expect a damping rate proportional to the size of the frozen spin moment. However, the measured values of $\sigma \approx 0.04{-}0.07\mu\text{s}^{-1}$ in Fig. 2 are relatively small. A typical muon $f$-electron hyperfine field in actinide systems is about $H_{\text{hyp}} \approx 1$ kOe$/\mu_{\text{B}}$, so that a damping rate corresponding to the lower limit for the ordered moment in $\delta$-Pu from neutron scattering (0.04-0.4 $\mu_{\text{B}}$) yields $\sigma \approx \gamma_\mu H_{\text{hyp}} = 3.4 - 34\mu\text{s}^{-1}$, orders of magnitude larger than the measured values. Finally, spin freezing of any sort (ordered or disordered) generally produces a damping rate which strongly increases with decreasing temperature. This, too, is not observed, indicating either a very small ordering temperature produced by tiny moments or very weak interatomic exchange [8]; other scenarios are mentioned below.

In higher applied fields one can resolve the Ti and Pu precession signals with sufficient accuracy to yield the muon Knight shift, and, hence, a measure of the local spin susceptibility. The Knight shift is defined as $K = (\nu - \nu_0)/\nu_0$, where $\nu$ is the measured frequency and $2\pi\nu_0 = \gamma_\mu H_0$, where $\gamma_\mu$ is the muon's gyromagnetic ratio ($8.51 \times 10^8$ Hz/T). Generally, $K = K_0 + K_{\text{dem}} + H_{\text{hyp}}\chi_f(T)/N_A\mu_B$, where $K_{\text{dem}}$ is the shift caused by the demagnetization fields, $\chi_f$ is the temperature-dependent f-electron susceptibility and $K_0$ is the shift from temperature-independent sources. The constants $N_A$ and $\mu_B$ are Avogadro's number and the Bohr magneton, respectively. $K_{\text{dem}} = 4\pi(\frac{1}{3} - N)\rho_{\text{mol}}\chi$, where $\rho_{\text{mol}}$ is the molar density and $N$ is the geometrical demagnetization factor. The latter is about 0.95-0.98 for our samples.

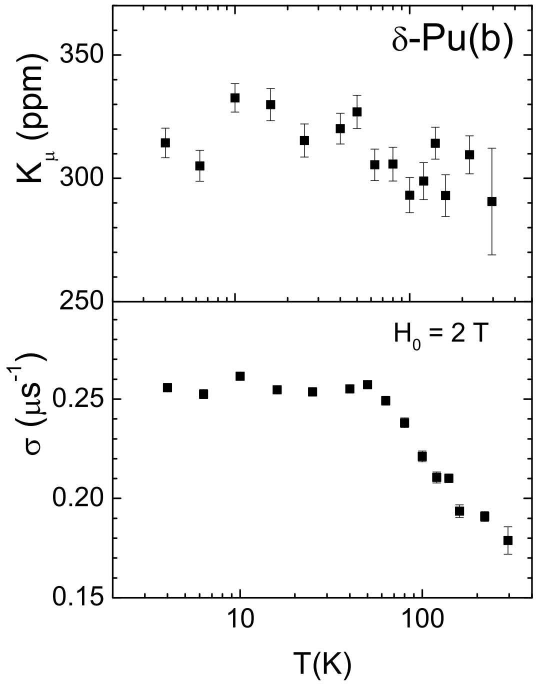


Fig. 3. Temperature dependence of the (top) Knight shift $K_\mu$ (see text) and (bottom) Gaussian linewidth $\sigma$ for $H_0 =$ 2.0 T in $\delta$-Pu(b). The temperature independent shift and linewidth below about 60 K is consistent with no ordered or disordered $f$-electron spin freezing. Muon diffusion likely accounts for the linewidth narrowing above about 60 K.

The absolute reference frequency $\nu_0$ is in principle obtained from the known Knight shift of the background material, in this case Ti ($K_{\text{Ti}}$). To our knowledge $K_{\text{Ti}}$ has not been measured. However, the muon Knight shifts of almost all metals which have been measured lie between +50-100 ppm [10], so we have taken $K_{\text{Ti}} \approx 75 \pm 25$ ppm in correcting our data.

The measured $K_\mu = K - K_{\text{dem}}$ for $\delta$-Pu(b), corrected for the Ti shift, is shown in Fig. 3, together with the TF linewidth $\sigma$. For comparison, corresponding data [8] for $\alpha$-Pu are shown in Fig. 4. The decrease in linewidth above about 60 K in $\delta$-Pu(b) suggests that the muon begins to diffuse above that temperature, causing motional narrowing. This is observed in $\alpha$-Pu [8], where the linewidth first decreases as the muon diffuses locally, and then

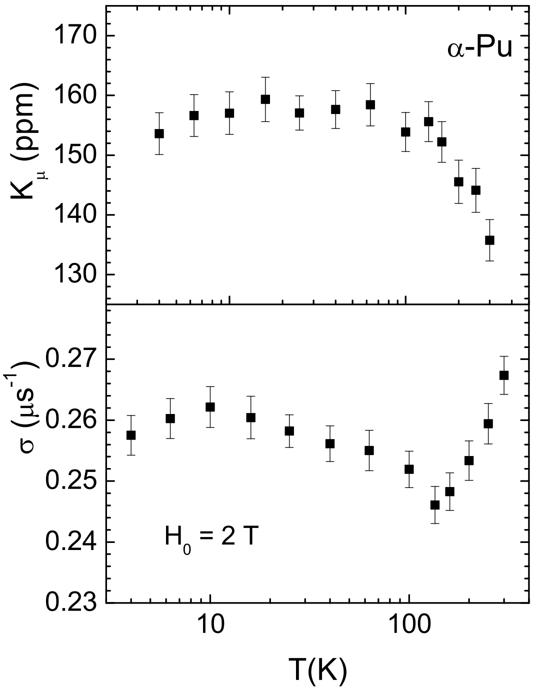


Fig. 4. Temperature dependence of the (top) Knight shift $K_\mu$ (see text) and (bottom) Gaussian linewidth $\sigma$ for $H_0 =$ 2.0 T in $\alpha$-Pu. The observed temperature dependencies in $K_\mu$ and $\sigma$ above about 100 K are qualitatively explained in terms of muon diffusion [8]

increases (accompanied by a change in $K_\mu$) as the muon probably diffuses to the vicinity of the Fe impurities where the net hyperfine field is changed. Rapid muon diffusion in metals and compounds above 100 K is not uncommon [11]. The important feature of the data in $\delta$-Pu(b), however, is that neither the linewidth nor the Knight shift show any measurable temperature dependence at low temperatures, where magnetic order might be anticipated.

The magnitude of $K_\mu \approx 320$ ppm is roughly consistent with NMR shifts measured in a $\delta$-Pu sample with 5.0 at. % Ga [12,13]. In the NMR experiments the hyperfine field was estimated to be 2.8 kOe/$\mu_{\rm B}$ and the Knight shift varied between about 500 - 700 ppm. We cannot determine the value of $H_{\rm hyp}$ from our data because of the lack of temperature dependence in $K_\mu$. ($H_{\rm hyp}$ is found from the slope on a plot of $K(T)$ vs. $\chi(T)$, with T an implicit variable.) Nevertheless, as stated above, $H_{\rm hyp}$ is typically $\approx 1$ kOe/$\mu_{\rm B}$ in other actinide materials, yielding reasonable agreement with the NMR shift magnitudes. In contrast to the NMR data, however, where the Knight shift increases almost 40% below 100 K, we find no appreciable temperature dependence for $K_\mu$ below 100 K. The magnitude of $\sigma$ is broadened compared to the lower-field data in Fig. 2 by a distribution of anisotropic Knight shifts in the polycrystalline sample of width $\delta K \approx |K|$, so that $\sigma \approx \gamma_\mu H_0|K|$.

The temperature-independent behavior of the muon Knight shifts and linewidths at low temperatures shown in Figs. 3 and 4 is in contrast to the increases in the bulk susceptibilities observed with decreasing temperature in both $\alpha$-Pu and $\delta$-Pu(b) (Fig. 1). A simple fit of the $\delta$-Pu(b) data to $\chi(T) = \chi_0 + \chi_{\rm CW}(T)$, where $\chi_0$ is independent of temperature and $\chi_{\rm CW}(T)$ is the usual Curie-Weiss susceptibility, yields $\chi_0 = 725(10)$ $\mu$emu/mol-Pu with an effective moment $\sim 0.23$ $\mu_{\rm B}$. By contrast a similar fit to $\delta$-Pu(a) yields $\chi_0 \sim 517(8)$ $\mu$emu/mol-Pu, with a much smaller effective moment, depending on how one fits the low-temperature peak. An effective moment of $\sim 0.2\mu_{\rm B}$ on each Pu atom (or on each Ga atom) with a minimum spin 1/2 would result in a temperature-dependent $\mu$SR transverse-field linewidth [19] much larger than the measured values in 2T applied field below about 20 K, as discussed previously[8]. This is not observed. Usually a low-temperature increase in $\chi$, when not reflected in the Knight shift, signifies very dilute impurity moments which are not intrinsic to the material under study, in this case Pu. However, we do not at present understand the differences in the $\chi(T)$ between $\delta$-Pu(a) and $\delta$-Pu(b).

## 4. Conclusion

Our results set an upper limit for either the ordered or disordered frozen spin moment for the $f$-electrons in Ga-stabilized $\delta$-Pu: $\mu_{\rm ord} \leq 10^{-3}\mu_{\rm B}$. Note that we do not specify that there are no localized moments in $\delta$-Pu, only that they do not freeze above T = 4 K. One possible reason for not finding evidence of local moments with $\mu$SR is that the spins are fluctuating at an exchange frequency $\omega_e$ which is large enough to completely motionally narrow the dynamical linewidth in the time scale of our measurements. In Ref. [8] we use a mean-field estimate to establish that such motional narrowing would occur only if $\omega_e > 10^{12} - 10^{13}$ s$^{-1}$ at T = 4 K for a hypothetical $f$-electron moment of 1 $\mu_{\rm B}$. Values of $\omega_e$ smaller than this would yield a mean-field estimate for the Néel temperature significantly $> 2.2$ K, inconsistent with the temperature-independence of our linewidths at low temperatures.

Theoretical attempts to explain the lack magnetism in $\delta$-Pu have included approximate cancelation of the spin and orbital moments [14], and noncollinear intra-atomic magnetism [15], neither of which is likely in view of our measurements. A very high Kondo temperature [16] could explain the results, as well as recent calculations which predict an essentially filled $f^6$ $J = 5/2$ spin-orbit split ground state [17,18].

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