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Journal of Alloys and Compounds 444–445 (2007) 80–83

Journal of ALLOYS AND COMPOUNDS

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The search for magnetic order in δ-Pu metal using muon spin relaxation

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Received 23 October 2006; received in revised form 1 December 2006; accepted 5 December 2006
Available online 29 January 2007

Abstract

We review results from previous muon spin relaxation (μSR) 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 δ-Pu (4.3 at.% Ga) of $\mu_{\rm ord} \leq 10^{-3}\mu_{\rm B}$. In addition, we present new data in $H_0 = 0.25$ and 2 T applied field on a highly annealed δ-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.

Keywords: 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 recently taken root outside of the small 'Pu community' with the discovery of superconductivity in $PuMGa_5$, M = Co [3] and 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 δ 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 α-phase of Pu, where the f-electrons are itinerant. The theoretical localization of δ-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 δ-Pu, citing a limit for the ordered moment from neutron scattering of between 0.04 and 0.4$\mu_{\rm B}$ [7].

Against this background, we began a study of both α-Pu and δ-Pu (4.3 at.% Ga) in 2004 using the muon spin relaxation technique (μSR). μSR is particularly suitable for this task because of its high sensitivity to small-moment magnetism, wherein ordered moments as small as 0.001 $\mu_{\rm B}$ 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,

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2006.12.026

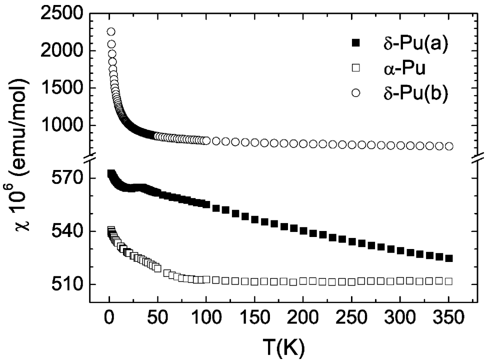

Fig. 1. Temperature dependence of the static susceptibility in 2 T applied field for the two measured δ-Pu samples: (a) annealed for 43 h at 440 °C and (b) annealed for 200 h at 465 °C. For comparison the susceptibility of α-Pu is also shown.

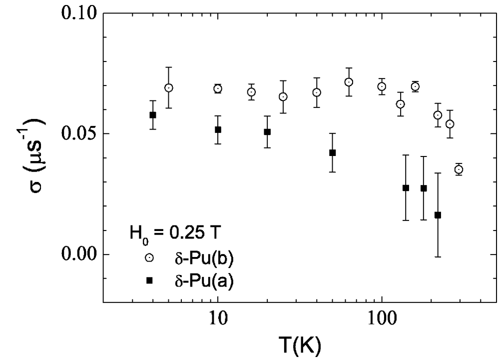

Fig. 2. Temperature dependence of the Gaussian damping rate σ in δ-Pu (a) and δ-Pu (b) in $H_0 = 0.25$ T applied field. The small, relatively temperature-independent magnitude of σ is consistent with no ordered or disordered f-electron spin freezing.

and, thus, μSR 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 δ-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 h at 440 °C, and is referred to as δ-Pu (a). The second δ-Pu (4.3 at.% Ga) sample was isotopically identical to the first, with the same impurity concentration, but was annealed for approximately 200 h at 465 °C. This sample, denoted δ-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 α-Pu. Data taken on δ-Pu (a) and α-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 μm thick Kapton coating and were placed inside a Ti cell under He atmosphere to prevent contamination. The cell possessed a thin 50 μm Ti window to allow the muon beam to enter. A negligible fraction of the beam stopped inside the Kapton or Ti window.

In a μ^+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. 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 μs. 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 ν and the damping rate of the precession signal σ, which is a measure of the inhomogeneous field distribution inside the sample.

The μSR 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 σ for measurements in $H_0 = 0.25$ T in δ-Pu (a) and δ-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 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 $\sigma \approx 0.04$–$0.07\ \mu s^{-1}$ in Fig. 2 are relatively small. A typical muon f-electron hyperfine field in actinide systems is about $H_{\rm hyp} \approx 1\ {\rm kOe}/\mu_{\rm B}$, so that a damping rate corresponding to the lower limit for the ordered moment in δ-Pu from neutron scattering (0.04–0.4 $\mu_{\rm B}$) yields $\sigma \approx \gamma_\mu H_{\rm hyp} = 3.4$–$34\ \mu s^{-1}$, 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 ν is the measured frequency and $2\pi\nu_0 = \gamma_\mu H_0$, where γ_μ is the muon's gyromagnetic ratio (8.51×10^8 Hz/T). Generally, $K = K_0 + K_{\rm dem} + H_{\rm hyp}\chi_{\rm f}(T)/N_A\mu_B$, where $K_{\rm dem}$ is the shift caused by the demagnetization fields, $\chi_{\rm f}$ is the temperature-dependent f-electron susceptibility and K_0 is the shift from temperature-independent sources. The constants $N_{\rm A}$ and $\mu_{\rm B}$ are Avogadro's number and the Bohr magneton, respectively. $K_{\rm dem} = 4\pi((1/3) - N)\rho_{\rm mol}\chi$, where $\rho_{\rm mol}$ is the molar density and N is the geometrical demagnetization factor. The latter is about 0.95–0.98 for our samples.

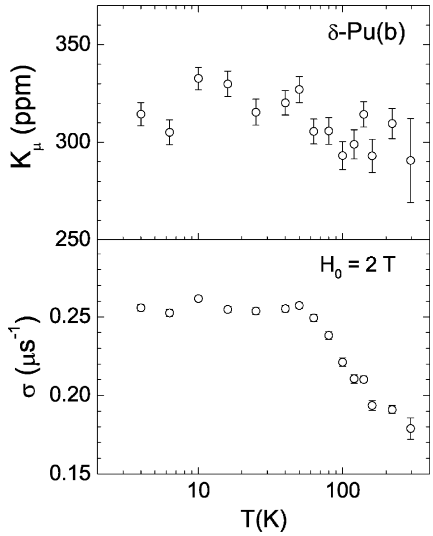

Fig. 3. Temperature dependence of the (top) Knight shift K_μ (see text) and (bottom) Gaussian linewidth σ for $H_0 = 2.0$ T in δ-Pu (b). The temperature independent shift and linewidth below about 60 K is consistent with no ordered or disordered f-electron spin freezing. Muon diffusion likely accounts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

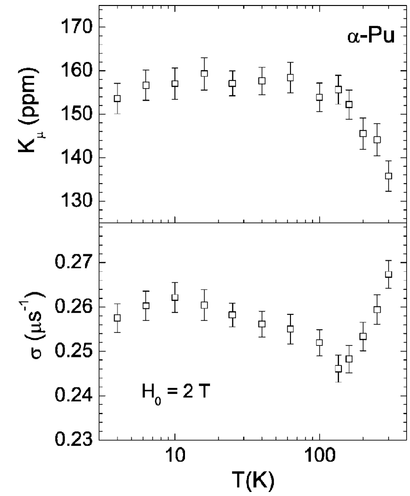

Fig. 4. Temperature dependence of the (top) Knight shift K_μ (see text) and (bottom) Gaussian linewidth σ for $H_0 = 2.0$ T in α-Pu. The data are from Ref. [8]. The observed temperature dependencies in K_μ and σ above about 100 K are qualitatively explained in terms of muon diffusion [8].

The absolute reference frequency ν_0 is in principle obtained from the known Knight shift of the background material, in this case Ti (K_{Ti}). To our knowledge K_{Ti} has not been measured. However, the muon Knight shifts of almost all metals which have been measured lie between +50 and 100 ppm [10], so we have taken $K_{\mathrm{Ti}} \approx 75 \pm 25$ ppm in correcting our data.

The measured $K_\mu = K - K_{\mathrm{dem}}$ for δ-Pu (b), corrected for the Ti shift, is shown in Fig. 3, together with the TF linewidth σ. For comparison, corresponding data [8] for α-Pu are shown in Fig. 4. The decrease in linewidth above about 60 K in δ-Pu (b) suggests that the muon begins to diffuse above that temperature, causing motional narrowing. This is observed in α-Pu [8], where the linewidth first decreases as the muon diffuses locally, and then increases (accompanied by a change in K_μ) 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 δ-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 δ-Pu sample with 5.0 at.% Ga [12,13]. In the NMR experiments the hyperfine field was estimated to be 2.8 kOe/μ_{B} and the Knight shift varied between about 500–700 ppm. We cannot determine the value of H_{hyp} from our data because of the lack of temperature dependence in K_μ. (H_{hyp} is found from the slope on a plot of $K(T)$ versus $\chi(T)$, with T an implicit variable.) Nevertheless, as stated above, H_{hyp} is typically ≈ 1 kOe/μ_{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_μ below 100 K. The magnitude of σ 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 α-Pu and δ-Pu (b) (Fig. 1). A simple fit of the δ-Pu (b) data to $\chi(T) = \chi_0 + \chi_{\mathrm{CW}}(T)$, where χ_0 is independent of temperature and $\chi_{\mathrm{CW}}(T)$ is the usual Curie–Weiss susceptibility, yields $\chi_0 = 725(10)$ μemu/mol Pu with an effective moment $\sim 0.23\,\mu_{\mathrm{B}}$. By contrast a similar fit to δ-Pu (a) yields $\chi_0 \sim 517(8)$ μemu/mol Pu, with a much smaller effective moment, depending on how one fits the low-temperature peak.

The dramatic differences in the magnetic susceptibility measurements are not currently understood. The primary difference between the annealing profiles of the two delta specimens is the longer annealing time of specimen δ-Pu (b), which is expected to significantly improve the homogenization of the Ga within the sample [14]. Thus, it may be that one effect of the homogenization is to alter the electronic structure of the specimen, effectively narrowing the conduction bands as reflected by the $\sim 40\%$ increase in χ_0. Alternatively, a Van-Vleck type susceptibility could be altered by a change in crystal fields produced by changes in the local Pu–Ga atom environment.

The observed low-temperature Curie tail could reflect developing moments on the Pu atoms nearest the Ga sites. However, an effective moment of $\sim 0.2\,\mu_{\mathrm{B}}$ on each Pu atom (or on each Ga atom) with a minimum spin 1/2 would result in a temperature-dependent μSR transverse-field linewidth [15] much larger than the measured values in 2 T applied field below about 20 K, as discussed previously [8]. This is not observed. Usually a low-temperature increase in χ, 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.

Although we do not at present understand the differences in $\chi(T)$ between δ-Pu (a) and δ-Pu (b), we note that the μSR low-field linewidths (Fig. 2) are significantly larger than the expected broadening from either the Pu nuclear moments (estimated to be $\approx 0.024\ \mu s^{-1}$) or the Ga nuclear moments (negligible), and thus may be reflecting a spread in χ_0 and, correspondingly, the approximately 40% increase in χ_0 in going from δ-Pu (a) to δ-Pu (b). Specific heat measurements on one alloy composition with a series of annealing profiles would be helpful to answer these questions more definitively.

4. Conclusion

Our results set an upper limit for either the ordered or disordered frozen spin moment for the f-electrons in Ga-stabilized δ-Pu: $\mu_{\rm ord} \leq 10^{-3}\ \mu_{\rm B}$. Note that we do not specify that there are no localized moments in δ-Pu, only that they do not freeze above $T = 4$ K. One possible reason for not finding evidence of local moments with μSR is that the spins are fluctuating at an exchange frequency $\omega_{\rm e}$ which is large enough to completely motionally narrow the dynamical linewidth in the time scale of our measurements. This was briefly discussed previously [8], where we estimated a mean-field lower limit [16] for $\omega_{\rm e}$ in the paramagnetic state set by the measured values of our temperature-independent zero-field linewidths in Fig. 2. We find that motional narrowing will occur only if $\omega_{\rm e} > 10^{11} - 10^{12}\ {\rm s}^{-1}$ at $T = 4$ K for a hypothetical f-electron moment of $1\ \mu_{\rm B}$. Values of $\omega_{\rm e}$ greater than this yield a mean-field estimate for the Néel temperature significantly > 4 K, inconsistent with the temperature-independence of our linewidths at low temperatures. Thus, within this simple picture, the value of $\omega_{\rm e}$ is confined to a rather narrow range by our data; too small and we would see dynamical broadening at low temperature, too large and the system magnetically orders. More likely scenarios are that the f-electron moment is much smaller than $1\ \mu_{\rm B}$ or the interatomic exchange is much weaker than the mean-field estimate.

Theoretical attempts to explain the lack of magnetism in δ-Pu have included approximate cancelation of the spin and orbital moments [17], and noncollinear intra-atomic magnetism [18], neither of which is likely in view of our measurements. A very high Kondo temperature [19] could explain the results. Recent calculations using the 'around mean-field' version [20] of the local density approximation, plus on-site correlations for the f-electrons (LDA + U), predict a non-magnetic ground state, but fail to reproduce the finite density of states at the Fermi energy observed in photoemission spectroscopy. The f-electron occupation in the $J = 5/2$ ground state multiplet in this calculation is $n_{\rm f} = 5.44$. An apparent theoretical step closer to the actual situation adds dynamical correlations to the LDA + U theory, and predicts a non-magnetic ground state with $n_{\rm f} = 5.8$; so-called 'spin-orbit fluctuations' yield a finite density of states at the Fermi surface [21]. Experimentally, specific heat measurements in Am-doped δ-Pu, which possesses an expanded lattice parameter, show no evidence for either a magnetic ground state or an increase in the electronic density of states at the Fermi surface with Am doping, suggesting that the system is close to a filled, non-magnetic f^6 shell, where hybridization with non f electrons yields the enhanced Sommerfeld coefficient in δ-Pu [22].

Acknowledgments

Work at LANL and LLNL (contract W-7405-Eng-48) performed under the auspices of the U.S. D.O.E. Work at Riverside supported by the U.S. NSF, Grant DMR-0102293. We thank the staff of TRIUMF for their kind assistance and acknowledge helpful discussions with G. Lander, P.M. Oppeneer, J.D. Thompson and F. Wastin.

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