Journal of Nuclear Materials 385 (2009) 35–37

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Pu neutron scattering studies – Magnetism and structure

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A B S T R A C T

Neutron scattering results are presented on δ-phase Pu stabilized with 2% Ga performed on the time-of-flight instrument Pharos in zero magnetic field and also in an 8 T applied field over the temperature range from room temperature down to 1.7 K. Comparison of the field and temperature dependence of the diffraction patterns showed no evidence of peaks of magnetic origin, and thus no long-range order is induced even in an 8 T applied field. Due to the wave-vector character of the scattering, this result can not be explained by the possible cancellation of the orbital and spin components of the moment. Additional inelastic scattering experiments at room temperature did reveal a very weak inelastic feature at 90 meV which is tempting to ascribe to H impurities. However, the feature did not have the expected Q^2 intensity dependence as would be expected for H vibrations, and thus the origin of this 90 meV peak is unexplained.

1. Introduction

In this paper we present recent neutron elastic and inelastic scattering results on plutonium in order to further investigate the lingering question of the nature of the magnetism in this element. Several theoretical calculations have predicted the occurrence of an ordered magnetic moment between 0.25 and 5 μ_B. In large measure the occurrence of a localized moment is driven by the requirement that the theory properly account for the ≈25% volume change between α- and δ-phases, as reviewed in [1].

A large body of experimental work in the period 1960 to the present has in general found no evidence for a static magnetic moment at low temperature of the magnitude predicted by theory. As discussed in the comprehensive review by Lashley et al. [1], the bulk properties measurements have included heat capacity, magneto resistivity, NMR, and magnetic susceptibility. Although some of these results revealed unexplained artifacts that could be ascribed to magnetism, nearly all were later ruled out as resulting from sample contamination or alternate interpretations of the data. A recent paper [2] reporting μ_{SR} results on δ-stabilized Pu (4.3% Ga) placed a lower limit on an ordered or frozen moment of $\leqslant 10^{-3}$ μ_B.

At least three possibilities exist for the occurrence of magnetism in Pu: (1) Ordered antiferromagnetism in which there is partial or total cancellation of the ordered moment at $Q = 0$ due to oppositely directed spin and orbital angular moment components. A similar situation does exist in the rare earth element Sm, in which case no net magnetic moment would be measured with a conventional bulk magnetic probe such as squid magnetometry. However, as outlined below neutron diffraction would certainly observe the moment through the form factor assuming it were not too small to be detected (with proper background suppression the minimum detectable moment is ≈0.4 μ_B for ferromagnetism and as little as 0.1 – 0.2 μ_B for antiferromagnetism). (2) The second possibility is that the magnetism exhibits only short range correlations, either static or fluctuating in time. This is similar to the behavior observed in spin glass systems, which show large applied field sensitivity. In particular, magnetization curves measured on warming from a zero field cooled state are vastly different from those measured in cooling in the presence of a field. This phenomenon has not been observed in Pu. The neutron scattering measurements presented in this paper in applied fields up to 8 T are again designed to explore a possible cluster or short range magnetism. Previous limited *bulk* magnetization measurements did not indicate field-induced *ferromagnetic* order. (3) The third possibility for magnetism is that of a dynamic fluctuating magnetization with a time scale of order nanoseconds or faster. Such a fluctuating system would again not have a clear signature in most of the bulk measurements to date, but would have a possibility of observation via quasi-elastic neutron scattering. This is essentially the broadening of the Bragg peaks in energy (time) space analogous to the small cluster broadening of Bragg peaks in wave-vector (particle size) space. Experiments are planned at the Lujan Center to investigate this possibility of a temporal fluctuation in the antiferromagnetic moment.

2. Previous neutron scattering results

Time of flight neutron diffraction measurements were performed [3] in the 1990s on 95% enriched ^{242}Pu. This isotope has

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doi:10.1016/j.jnucmat.2008.09.052

the advantage of relatively low absorption (σ_{abs} = 18.5 barns) compared to σ_{abs} = 1017 barns for ^{239}Pu (values for 1 A). Neutron scattering experiments on samples of highly absorbing materials essentially sense only the atoms in a relatively thin surface layer, thus nullifying one of the unique features of neutron scattering, the ability to sense atomic and magnetic ordering in bulk 3-dimensions. Absorption limitations can be mitigated by using sample containers consisting of the annulus between two concentric cylinders; however this does not eliminate the possibility of surface effects that are not representative of the bulk material.

Fig. 1 illustrates a diffraction pattern on 95% enriched ^{242}Pu [3] taken on the HIPD diffractometer at the Lujan Center. The figure shows (a) the diffraction data, (b) a calculated profile using the model of Kutepov and Kutepova [4] that predicts a static ordered antiferromagnetic moment 2.4 μ_B for the δ-phase. Note that this model requires sizable magnetic diffraction peaks in the d-spacing range 3.5 – 5 A, which are clearly unobserved in the experimental data (also easily seen in the difference plot labeled K&K between the data and the model intensities). The dotted line is the calculated magnetic form factor [5] for Pu^{3+} which exhibits a peak at a finite value of $Q = 2\pi/d$ rather than at $Q = 0$ (outside the data range of Fig. 1) characteristic of a ferromagnet. Similar low-temperature results were found for δ-phase ^{242}Pu (stabilized with 5% Al) again illustrating the absence of magnetic peaks above the instrumental threshold sensitivity of approximately 0.3 – 0.4 μ_B.

Another null result for magnetism was obtained from the elastic/inelastic data on a polycrystalline sample of Al-stabilized δ-phase $^{242}Pu_{0.95}Al_{0.05}$ published by McQueeney et al. [6]. These experiments designed to elucidate the phonon density of states were also integrated over the low-Q range ($0.75 < Q < 2$ A^{-1}) and at temperatures down to 27 K showed no inelastic component that could be ascribed to magnetic excitations. The data perfectly fit the low-Q model for phonons with no statistically relevant residuals.

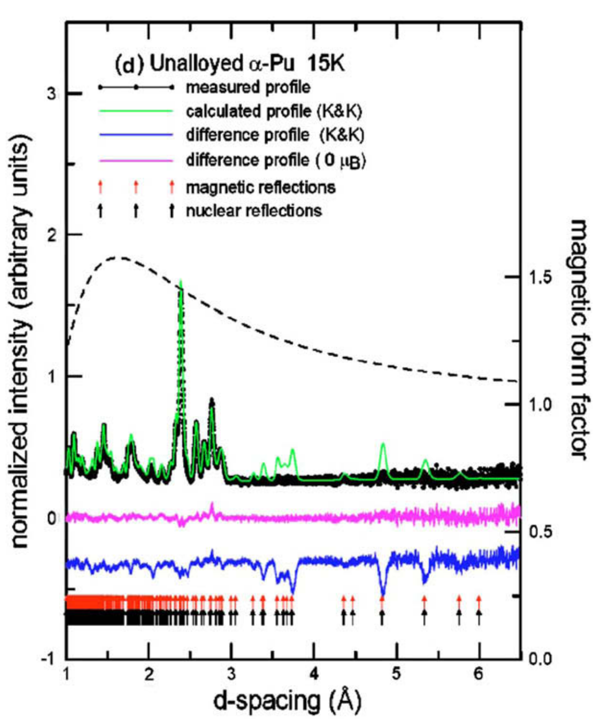

Fig. 1. Diffraction data on unalloyed α-phase ^{242}Pu enriched to 95% at 15 K. The solid line through the data is the calculated profile using the model of Kutepov and Kutepova [4] clearly illustrating the absence of antiferromagnetic peaks predicted by the theory. The dotted line is the calculated magnetic form factor [5] for Pu^{3+}.

3. Neutron scattering results in an applied magnetic field

In order to investigate the possibility of an applied field-induced component to the magnetism in Pu, elastic and inelastic scattering data were taken on the Pharos spectrometer at the Lujan Center on ^{242}Pu stabilized in the δ-phase by addition of 2% Ga. The measurements were made in fields up to 8 T applied using a split-pair superconducting solenoid, and covered the temperature range from room temperature down to 1.7 K. This study was undertaken to study the possibility that the magnetic moments were only weakly coupled in zero field and that long-range order could be induced by the application of an applied field at low-T. Also these results would also reveal any potential spatial inhomogenieties in the spin order (e.g., weakly coupled clusters or micro-domains) that could be coalesced or ordered by the application of a field.

While designed to study inelastic processes, Pharos also records the elastic (no energy transfer) channel as well for all Q values sampled. Thus both conventional diffraction data are available as well as inelastic results. The data are shown in Figs. 2 and 3 taken in 0 applied field and in an 8 T applied field. Results are shown for room temperature and at 1.7 K. The low-T data in 0 field were divided into the 8 T data to examine any changes in the scattering occurring with the application of the field. As shown in Fig. 3 a null result was found, indicating no field-induced features within the statistical sensitivity of the instrument. This includes both the elastic diffraction data as well as the inelastic spectrum over the range 5 meV to 100 meV. Likewise no additional scattering peaks were seen in the elastic (diffraction) component when the low-T data were compared to room temperature.

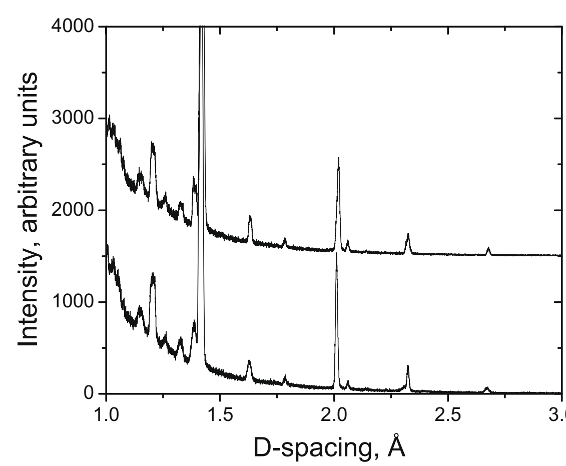

Fig. 2. Stacked data plot of diffraction patterns showing essentially identical results at 300 K with no magnetic field applied (upper curve), and at 1.7 K in an 8 T applied field (lower). The vertical scale of the upper plot is displaced by 1500 units.

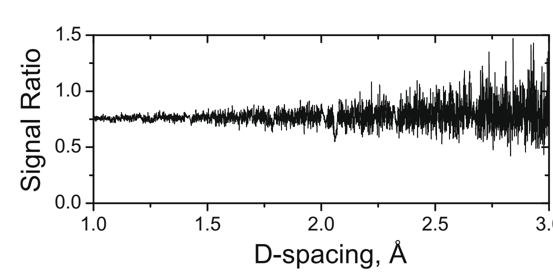

Fig. 3. Ratio of diffraction intensity taken at 4 K in zero field and with an 8 T vertical field applied.

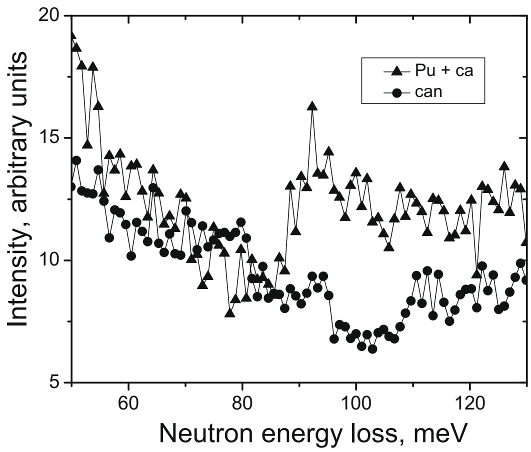

Fig. 4. Inelastic scattering from 2% Ga ^{242}Pu at 300 K using an incident neutron energy 200 meV. The feature at 90 meV is unexplained (see text).

Additional inelastic scattering experiments were performed on Pharos at room temperature to examine possible dynamic scattering processes. Using incident energy of 200 meV, a very weak inelastic feature was observed at 90 meV as shown in Fig. 4, which is tempting to ascribe to H impurities. However, the feature did not have the expected Q^2 intensity dependence (modified by a Debye – Waller factor) as would be expected for H vibrations, nor did it have an intensity dependence suggestive of a magnetic excitation Thus the origin of this 90 meV peak is unexplained.

The strong conclusion from the large body of experimental work is that there is no static ordered magnetic moment in Pu. Equally important is the concept that Pu exhibits an intermediate valence state involving a mixing of $5f^5$ and $5f^6$ electron states that leads to a *non-magnetic* ground state. Two recent theoretical papers [7,8] addressing the valence fluctuation phenomena both predict the absence of ordered magnetism and also account for the 25% $\delta - \alpha$ volume expansion and other features. The unpaired $5f$ electrons, however, would imply that the ground state will exhibit *dynamic spin fluctuations* on some time scale that could possibly be probed with neutron scattering. Such is the case in the analogous rare earth element Ce studied by Murani et al. [9,10] in α-Ce stabilized with 7% Sc for which a very broad inelastic spectral response, centered at 170 meV, was found. Similar measurements using very high incident neutron energies are planned for the inelastic chopper spectrometer at the Lujan Center. These studies are challenging since no a-priori information is available on the expected time scale to use as a guide for the expected excitation energy or its energy width. The availability of single crystals would be a significant asset in this and other neutron scattering studies in Pu.

Acknowledgement

The authors have benefitted from many informative discussions with Angus Lawson and Gerry Lander on topics related to magnetism in plutonium.

References

[1] J.C. Lashley, A. Lawson, R.J. McQueney, G.H. Lander, Phys. Rev. B 72 (2005) 54416.
[2] R.H. Hefner, G.D. Morris, M.J. Fluss, B. Chung, D.E. MacLaughlin, L. Shu, J.E. Anderson, Physica B 374&375 (2006) 163.
[3] A.C. Lawson, B. Martinez, R.B. von Dreele, J.A. Roberts, R.I. Shelton, T.O. Brun, Philos. Mag. B 80 (2000) 53.
[4] A.L. Kutepov, S.G. Kutepova, J. Phys. Condens. Matter 15 (2003) 2607.
[5] G.H. Lander, in: K.A. Gschneidner, L. Eyring, G.H. Lander, G. Choppin (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 17, Elsevier, Amsterdam, 1993, p. 635.
[6] R.J. McQueeney, A.C. Lawson, A. Migliori, T.M. Kelly, B. Fulz, M. Ramos, B. Martinez, J.C. Lashley, S.C. Vogel, Phys. Rev. Lett. 92 (2004) 146401.
[7] L.V. Pourovskii, M.I. Katsnelson, A.I. Lichtenstein, L. Havela, T. Gouder, F. Wastin, A.B. Shick, V. Drchal, G.H. Lander, Europhys. Lett. 74 (2006) 479.
[8] J.H. Shim, K. Haule, G. Kotliar, Nature Lett. 446 (2007) 513.
[9] A.P. Murani, S.J. Levett, J.W. Taylor, Phys. Rev. Lett. 95 (2005) 256403.
[10] A.P. Murani, Z.A. Bowden, A.D. Taylor, R. Osborn, W.G. Marshall, Phys. Rev. B 48 (1993) 13981.