ELSEVIER

Journal of Alloys and Compounds 271–273 (1998) 463–466

Journal of ALLOYS AND COMPOUNDS

Magnetic order in NpO_2 and UO_2 studied by muon spin rotation

W. Kopmann[a,*], F.J. Litterst[a], H.-H. Klauß[a], M. Hillberg[a], W. Wagener[a], G.M. Kalvius[b], E. Schreier[b], F.J. Burghart[b], J. Rebizant[c], G.H. Lander[c]

[a]*Institut für Metallphysik und Nukleare Festkörperphysik, TU Braunschweig, D-38106 Braunschweig, Germany*
[b]*Physik-Department, TU München, D-85747 Garching, Germany*
[c]*European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*

Abstract

Muon spin rotation/relaxation (μSR) measurements were carried out in zero applied field on NpO_2 and UO_2 above and below their transition temperatures of 25 and 30.8 K, respectively. In NpO_2, a spontaneous spin precession pattern is observed for $T<25$ K. The data are compared to analogous results on isostructural UO_2 where the 30.8 K transition is well established as the Néel temperature for antiferromagnetic order. The μSR patterns are, in their basic features, quite alike for the two compounds. This establishes unambiguously that the transition at 25 K in NpO_2 is basically of magnetic origin. The ordered moment on Np is estimated to be smaller than about 0.15 μ_B, i.e. less than 10% of the moment on U in antiferromagnetic UO_2. © 1998 Elsevier Science S.A.

Keywords: μSR; NpO_2; UO_2; Magnetism

1. Introduction

NpO_2 and UO_2 are nearly insulating semiconductors crystallizing in the cubic CaF_2 structure. The high-temperature magnetic susceptibilities are fully compatible with the $^4I_{9/2}$ ($5f^3$) and $^3H_4$ ($5f^2$) Hund's rule ground states for Np^{4+} and U^{4+} in NpO_2 and UO_2, respectively. The presence of a Np^{4+} ion in NpO_2 is safely established by the Mössbauer isomer shift [1], even at low temperatures, which rules out any discussion in terms of a non-Kramers Np^{3+} ion.

Susceptibility, resistivity and specific heat measurements (see Ref. [2] and references given therein), as well as Mössbauer spectroscopy [3,4] on NpO_2 establish a transition at 25 K. Its exact nature has, however, been enigmatic, especially since neither neutron (see references in Ref. [2]) nor Mössbauer data could prove the existence of an ordered magnetic state. In fact the Mössbauer spectra for $T<25$ K are not incompatible with the presence of magnetic order [3] but, if so, require that the moment at the Np ion has to be extremely small (<0.02 μ_B). In Ref. [4] it was concluded that the transition is more likely to be structural. Similarly, the behaviour of the neutron inelastic cross-section at low temperatures was interpreted [2] as a consequence of a collective Jahn-Teller distortion of the oxygen sublattice.

The first order transition at $T_N=30.8$ K in UO_2 is well established as the Néel temperature of a type I antiferromagnet with 1.74 μ_B as saturated moment [5]. The spin structure has finally been determined to be of a 3k type [6]. Although a small volume change ($\sim 10^{-5}$) occurs at T_N, the cubic unit cell is maintained. A detailed theoretical analysis of magnetic structure and distortion can be found in Ref. [7]. The results of inelastic neutron scattering performed for investigation of the crystalline electric field splitting are reported in [8].

2. Experimental

In μSR spectroscopy spin-polarized positive muons (μ^+) are implanted into the sample to be studied. The μ^+ come to rest at interstitial sites. Parity violation in weak interaction causes a sizeable backward–forward (b–f) asymmetry for the emitted positrons along the direction of the muon spin at the moment of muon decay. The time dependence of the b–f positron countrate asymmetry is recorded as the μSR spectrum. If the muon senses at its site a magnetic field, e.g. from surrounding dipoles, its spin will perform a precessional motion, which is seen as a sinusoidal temporal modulation of the b–f asymmetry. In the absence of an external field, the local fields in a

*Corresponding author. Fax: +49 531 3915129; e-mail: w.kopmann@tu-bs.de

PII S0925-8388(98)00112-1

paramagnet are randomly distributed in their spatial direction resulting in an incoherent muon spin precession. This leads merely to a decay of asymmetry with time. In an ordered magnet a resultant local field is present which is proportional to local magnetization, which causes coherent spin precession and in consequence a sinusoidal modulation of b–f asymmetry is observed in zero applied field (spontaneous precession pattern). This is a safe signature that magnetic order is present. The temperature dependence of the precession frequencies follows (with minor corrections) that of the spontaneous magnetization. Details of the shape of the μSR spectra depend on the distribution and the dynamic properties of the internal field (static and dynamic muon spin relaxation). The intricacies of μSR spectroscopy can be found, for example, in Ref. [9]. The major strength of μSR is its high sensitivity, which allows detection of magnetic moments even in the 10^{-3} μ_B range. The resolution is such that a rather substantial distribution in local field can be tolerated before the signal is lost altogether.

μSR spectroscopy on actinides has been reported mainly for U compounds (especially highly correlated systems such as heavy fermion compounds). Until now, only one study has been published for an intermetallic Np compound [10]. There is, however, no basic restriction for the application of μSR to transuranic materials. The problems are the fairly large amount of material needed and the required safety procedures.

The present μSR studies were carried out at the Paul-Scherrer-Institute (PSI), Switzerland, using a decay muon beam. The powder samples (~2 g) were doubly encapsulated in aluminum cylinders. These were sealed with indium and epoxy, respectively, under a ^{4}He atmosphere to ensure thermal contact. A ^{4}He and a ^{3}He cryostat allowed for variable sample temperatures between 0.3 K and room temperature. The fairly massive double encapsulation stops a sizeable portion of muons. This, in consequence, produces a substantial background signal in the μSR spectra recorded. To separate this background from the true sample signal, detailed 'dummy' studies with the sample containers were performed. The background signal consists of a b–f asymmetry with constant asymmetry and a weak Gaussian damping at all temperatures as expected for aluminum. In particular the containers will not generate a spontaneous μSR precession pattern.

3. Results

In Fig. 1, zero field μSR spectra of NpO_2 above and below the 25 K transition are shown. The appearance of a spin precession signal, in addition to a monotonously damped non-oscillating signal, is clearly visible for $T<25$ K. Data analysis showed that the precession signal contains probably two frequencies. The signal having the lower frequency is strongly dominant. Its temperature dependence is presented in Fig. 2.

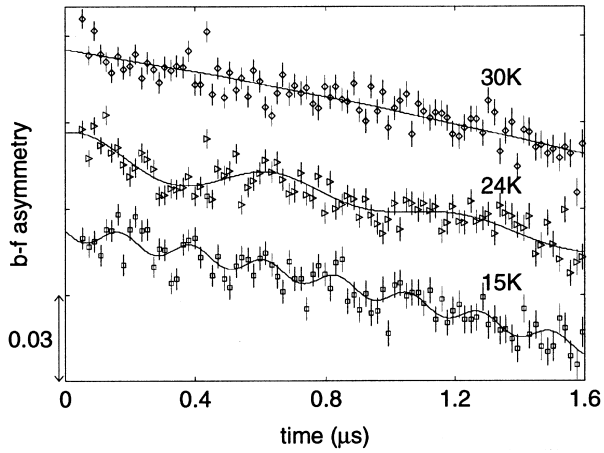

Fig. 1. NpO_2: b–f asymmetry at 15, 24 and 30 K and zero field.

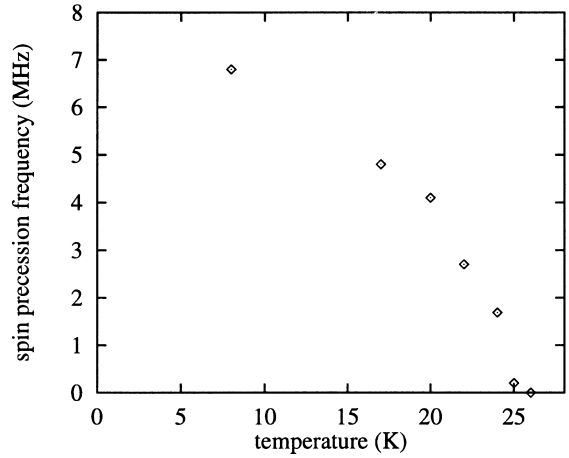

Fig. 2. NpO_2: temperature dependence of spin precession frequency.

A typical zero field μSR spectrum for antiferromagnetic UO_2 ($T<30.8$ K) is depicted in Fig. 3. The oscillating

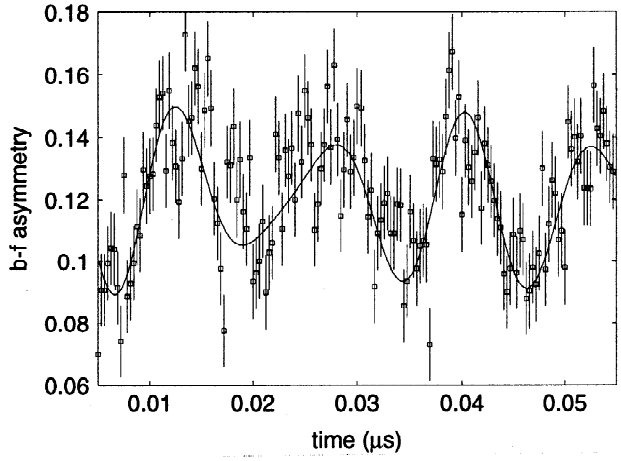

Fig. 3. UO_2: b–f asymmetry at 6.2 K and zero field.

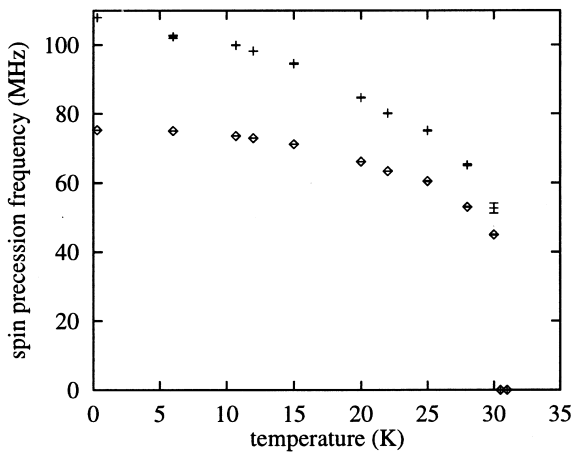

Fig. 4. UO_2: temperature dependence of spin precession frequencies.

signal portion is divided into at least two signals with different frequencies, whose temperature dependence is shown in Fig. 4. Again the portion having the lower frequency is dominant.

4. Discussion

The appearance of a spontaneous muon spin precession signal is a safe indicator for the presence of ordered magnetism, hence the data of Fig. 1 prove unambiguously that the 25 K transition leads into a magnetic state. μSR gives no direct information on the spatial spin structure. If the stopping site of the muon is known (or can be inferred with some confidence), the field values and distributions extracted from the μSR spectra can be compared with calculated interstitial fields of dipolar origin due to surrounding magnetic moments of an assumed spin structure. This procedure, though tedious, is quite promising for the case of UO_2 with its known spin structure and is in progress. From the fact that the overall features of the μSR magnetic response have much in common for UO_2 and NpO_2 (although details are certainly different), one may draw the tentative conclusion that type I antiferromagnetic order is likely also for NpO_2. The ratio of spontaneous frequencies for $T \rightarrow 0$ in NpO_2 and UO_2 should basically reflect the ratio of ordered moments on the two actinide ions. When comparing the two low-frequency components this would lead to μ_{Np} smaller than about 0.15 μ_B in NpO_2, which is clearly larger than the limit obtained by Mössbauer spectroscopy. The reason for this discrepancy may be a different spin structure for NpO_2, which would mean that the here envisaged signals for both compounds are caused by different spin surroundings. If we compare, however, the low frequency component for NpO_2 with the second frequency found for UO_2 (see Fig. 4) only a μ_{Np} smaller than about 0.1 μ_B is found. In any case μ_{Np} is substantially reduced from the free ion value observed at high temperatures. Crystal field effects together with quadrupolar ordering as proposed in Ref. [11] cannot account for such a reduction of ordered moment [4] and the subject remains a challenge to theory.

The weak damping of the precession pattern in NpO_2 (Fig. 1), which is observed in UO_2 as well (Fig. 3), means that a rather well-defined antiferromagnetic structure is present in NpO_2. For example, incommensurate spin structures usually result in a rather strong damping [12], as does short-range magnetic order (see, for example, Ref. [13]).

The well-known first-order nature of the 30.8 K transition in UO_2 is visible in the sudden collapse of spontaneous frequencies (proportional to spontaneous magnetization) at T_N in Fig. 4. In NpO_2 (see Fig. 2) this type of behaviour is not present, the spontaneous frequencies (magnetization) behave as expected for a second-order magnetic phase transition.

Finally it should be emphasized that the presence of a non-precessing signal (as seen, for example, in Fig. 1) does not mean that only part of the sample is magnetically ordered. Some of the muons may occupy an interstitial site, where all contributions from neighbouring dipoles to the local field just cancel. This feature is not uncommon in type I antiferromagnetic structures (even in multi-k) for simple cubic lattices [14]. As stated, a more careful analysis of the data with the proper subtraction of the signal from the sample containers together with theoretical calculations of the local fields is in progress. It will not change the basic conclusions drawn here.

5. Conclusion

The appearance of a spin rotation pattern in the zero field μSR spectra of NpO_2 below 25 K establishes the transition to be magnetic. Comparison with analogous data for UO_2 confirm a greatly reduced ordered moment on Np (μ_{Np} smaller than about 0.15 μ_B or even smaller). It also indicates that the nature of the transitions in NpO_2 and UO_2 is different. The signature of a first-order transition is not present for NpO_2.

References

[1] B.D. Dunlap, G.M. Kalvius, in: A.J. Freeman, G.H. Lander (Eds.), Handbook Phys. Chem. Actinides, vol. II, Elsevier, Amsterdam, 1985, p. 329.
[2] G. Amoretti et al., J. Phys.: Cond. Matter 4 (1992) 3459.
[3] B.D. Dunlap et al., J. Phys. Chem. Solids 29 (1968) 1365.
[4] J.M. Friedt, F.J. Litterst, J. Rebizant, Phys. Rev. B 32 (1985) 257.
[5] J. Faber, G.H. Lander, Phys. Rev. B 14 (1976) 1151.

[6] P. Burlet et al., J. Less-Common Met. 121 (1986) 121.
[7] P. Gianozzi, P. Erdös, J. Magn. Magn. Mater. 67 (1987) 75.
[8] G. Amoretti et al., Phys. Rev. B 40 (1989) 1856.
[9] A. Schenck, Muon Spin Rotation Spectroscopy, Adam Hilger Ltd., Bristol and Boston, 1985.
[10] K. Aggarwal et al., Hyp. Interactions 64 (1990) 401.
[11] G. Solt, P. Erdös, J. Magn. Magn. Mater. 15,18 (1980) 57.
[12] L.P. Le et al., Phys. Rev. B 48 (1993) 7284.
[13] G.M. Luke et al., Phys. Rev. Lett. 73 (1994) 1853.
[14] L. Asch, Hyp. Interactions 64 (1990) 351.