Spin fluctuations of the uranium 5f-electrons in UN according to $^{14}$N-NMR data

Vasily V Ogloblichev$^1$, Stanislav V Verkhovskii$^1$, Aleksey M Potapov$^2$, Aleksandr Yu Germov$^1$, Almaz F Sadykov$^1$

$^1$M.N. Miheev Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620108 Russia

$^2$The Institute of High Temperature Electrochemistry, Ural Branch, Russian Academy of Sciences, Yekaterinburg, 620137 Russia

E-mail: ogloblichev@imp.uran.ru

Abstract. The results of the study of the paramagnetic region of uranium mononitride by the method of nuclear magnetic resonance (NMR) of $^{14}$N nuclei are presented. The $^{14}$N NMR spectra, the Knight shifts $K$, the spin-lattice relaxation times $T_1$ have been obtained within the temperature range $T = 60 – 375$ K and at magnetic fields 92.8 kOe and 117.5 kOe. The temperature dependence of the Knight shift of the $^{14}$N line is proportional to the spin susceptibility $\chi$ of 5f-electrons of uranium. The ratio of the experimentally determined value $TT_1K^2$ to the theoretically calculated value of the Korringa contribution is 21.5 (at $T = 295$ K), which is significantly more than for common metals. This suggests that nuclear relaxation is based on the same mechanism as the Knight shift, namely, the indirect connection between the $^{14}$N nuclei and the localized magnetic moments of uranium through conduction electrons. The experimental results on the $T$-dependence of the spin-lattice relaxation rate of $^{14}$N also do not contradict the assumption that uranium mononitride is a concentrated Kondo system.

1. Introduction

Properties of actinide compounds significantly depend on the degree of localization of 5f-electrons, which is usually characterized by the Hill’s criterion proposed in 1970 [1]. The latter is determined by the ratio between the average radius of the 5f-shell of the actinide atom to half the distance between the nearest actinides. The distance $D = 3.46$ Å [2, 3] between U-U in uranium mononitride (UN) is close to the critical value $D_c = 3.5$ Å of uranium compounds. Uranium mononitride is a representative of actinide compounds with metallic conductivity, in which 5f-electrons demonstrate local and band magnetism. For half a century, experimental and theoretical studies of actinide materials have focused on such behavior of 5f-electrons [4, 5, 6].

This study presents the features of the charge and spin state of uranium magnetic ions at the paramagnetic phase of uranium mononitride by nuclear magnetic resonance (NMR) spectroscopy using the $^{14}$N nuclei.

2. Samples and experimental procedure

The $^{14}$N NMR spectra, spin-lattice relaxation times $T_1$ have been obtained in the temperature range $T = 60 – 375$ K. Registration of NMR spectra were performed using an AVANCE III 500
Figure 1. $^{14}$N NMR spectra in the UN measured at a temperature $T = 295$ K at the external magnetic field 117.5 kOe. The inset shows the crystal structure of UN (NaCl-type).

and SXP 4-100 (Bruker) pulse NMR spectrometers equipped with superconducting magnets $H = 117.5$ kOe and 92.8 kOe, respectively.

The UN powder sample under study was a cylinder of 6 mm in diameter and a weight of 1.8 g. X-ray analysis of this sample has shown that UN has a cubic NaCl (space group $Fm\bar{3}m$ (225), inset in Figure 1) lattice with the unit cell parameter $a = 4.8981(8)$ Å (at $T = 295$ K). The obtained results are in agreement with the data from previous study [3].

The $^{14}$N NMR spectra were recorded using the spin-echo technique ($p - t_{del} - 2p - t_{del} -$ echo), the $p$-pulse duration was $p = 7$ µs, the delay between pulses was $t_{del} = 100$ µs. The spin-lattice relaxation time $T_1$ was measured by the method of inversion and subsequent recovery of nuclear magnetization. We used pulse sequence $2p - t_{inv} - p - t_{del} - 2p - t_{del} -$ echo with a constant delay of $t_{del} = 100$ µs and the time interval $t_{inv} = 0.01 - 2$ s. The recovery of nuclear magnetization was fitted by exponential dependence $M(t_{inv}) = M_0 - 2 \cdot M_0 \cdot \exp(-t_{inv}/T_1)$ [2, 7, 8]. $M_0$ is the equilibrium nuclear magnetization of the spin system.

Magnetization measurements were performed using SQUID-magnitometer MPMS (Quantum Design) in constant magnetic field up to 50 kOe at the temperature range from 2 K to 320 K.

Magnetization, NMR and X-ray diffraction data have been obtained from the same sample.

3. Experimental results and discussion

The $^{14}$N NMR spectrum of uranium mononitride is shown in Figure 1. The spectrum is satisfactorily described by symmetric gaussian line at $T = 295$ K. The nucleus of the isotope $^{14}$N has spin $I = 1$ and quadrupole moment $eQ = 0.0193 \times 10^{-24}$ cm$^2$ [9], however spectral splitting into two lines (due to transitions $m_I = +1 \leftrightarrow 0$ and $m_I = 0 \leftrightarrow -1$ does not occur due to the
The temperature dependence of the shift of the $^{14}\text{N}$ NMR line $K$ in UN is shown. On the inset inverse $K^{-1}$ dependence on the temperature is presented. The solid line is the result of the data approximation (see text).

The cubic structure of UN [7, 10].

The temperature dependence of the $^{14}\text{N}$ NMR line shift $K(T)$ is satisfactorily described by the dependence $K(T) = K_0 + C/(T - \theta_{\text{nmr}})$ (Figure 2). The temperature-independent contribution $K_0 = 0.050 (15)$ % is close to the Knight shift value of nitrogen in the metallic non-magnetic thorium mononitride $K(\text{ThN}) = 0.107(30)$ %. Absolute value of the characteristic temperature $\theta_{\text{nmr}} = -156(12)$ K within the error coincides with the Weiss constant determined from the temperature dependence of magnetic susceptibility $\chi(T)$.

The behavior of $\chi(T)$ is also satisfactorily described by the Curie-Weiss law, $\chi(T) = \chi_0 + C/(T - \theta)$, with the Weiss constant $\theta = -170(10)$ K, the Curie constant $C = 0.73(2)$ emu-K/mol and the temperature independent term $\chi_0 = 3.0 \times 10^{-4}$ emu/mol in the paramagnetic state. Effective electron magnetic moment of uranium is determined as $\mu_{\text{eff}} = 2.4(1)$ $\mu_B$ in the paramagnetic state.

The proportionality $K(T) \propto \chi(T)$ shows that the temperature-dependent contribution to the NMR line shift of nitrogen is due to the magnetism of 5$f$-electrons of uranium in the paramagnetic state of UN. The linear approximation of the $K(\chi)$ diagram leads to an estimate of the hyperfine constant value $H_{hf} = 2.6(2)$ kOe/$\mu_B$, which has the physical meaning of the effective hyperfine field created at the nitrogen nucleus by 5$f$-shells of the neighboring uranium atoms.

Spin-lattice relaxation data $T_1^{-1}$ of $^{14}\text{N}$ nuclei provide information about the low-frequency spin dynamics of $f$-electrons. When the temperature decreases from 375 K to 77 K the $T_1^{-1}$ value increases slightly (by 17%).

For non-transition nitrogen atoms surrounded by magnetic actinide atoms the spin-lattice relaxation rate of nuclear spins should be determined by two contributions [8]:
\[(T_1)^{-1} = (T_1)^{-1}_K + (T_1)^{-1}_f. \]  

(1)

The contribution \((T_1)^{-1}_K\) corresponding to Fermi contact interaction of conduction electrons and nuclear spins is determined by the well-known Korringa law \[12\]. In the free electron gas model it has the following form:

\[TT_1 K^2 = \frac{\hbar \gamma_e^2}{4\pi k_B \gamma_n^2},\]  

(2)

where \(K\) is the spin contribution to the NMR line shift, \(k_B\) is the Boltzman constant, \(\hbar = h/2\pi\) is Plank constant, \(\gamma_n\) and \(\gamma_e\) are the nuclear and electron gyromagnetic ratios, respectively. In our case, this value should be the following

\[(TT_1 K^2)_{\text{Korringa}} = 5.041 \times 10^{-5} \text{s-K},\]  

(3)

Experimentally obtained value \(TT_1 K^2\) at \(T = 295\) K is equal to

\[(TT_1 K^2)_{\text{Experiment}} = 10.82 \times 10^{-4} \text{s-K},\]  

(4)

in this case:

\[(TT_1 K^2)_{\text{Experiment}}/(TT_1 K^2)_{\text{Korringa}} = 21.5.\]  

(5)

The ratio (5) of the experimentally determined value \(TT_1 K^2\) to the theoretically calculated value of the Korringa contribution is higher than for the most of metals (usually 0.1 – 10) including non-magnetic ThP \((1.95 \pm 0.25)\) \[13\].

Moreover, the value \((^{14}T_1 T)^{-1}\) at \(T = 77\) K in UN is more than an order of magnitude greater than in ThN \[14\]. In ThN, the increase in the spin-lattice relaxation rate of nitrogen proportional to the temperature is due to the Korringa mechanism, i.e., the Fermi contact interaction with conduction electrons. Thus, the spin-lattice relaxation rate of \(^{14}\text{N}\) in the UN paramagnetic phase is determined by the contribution \((T_1)^{-1}_f\), which is due to the time-dependent isotropic part of the indirect hyperfine interaction of the \(^{14}\text{N}\) nucleus with \(5f\)-electrons of the actinide.

The contribution \((T_1)^{-1}_f\) can be written as \[2, 8\]

\[(T_1)^{-1}_f = \frac{2\mu_B}{\gamma_n^2 k_B H_{hf}}.\]  

(6)

Energy of spin fluctuations, \(\Gamma_{NMR}\), determines the relaxation rate of \(5f\)-electron spin of uranium.

A joint analysis of the results obtained has revealed the temperature dependence of the characteristic energy of spin fluctuations of the uranium \(5f\)-electrons: \(\Gamma_{NMR}(T) \propto T^{0.54(4)}\) (Figure 3). This behavior of \(\Gamma_{NMR}(T)\) is close to the temperature dependence of \(\Gamma_{NMR}(T) \propto T^{0.5}\) which is intrinsic to concentrated Kondo systems above the coherent state formation temperature \[8, 15\]. We believe that a large value \(\Gamma_{NMR} = 170(15)\) K at \(T = 295\) K is determined by the energy scale of the fluctuating valence state of the magnetic uranium ion in UN. Its ground state is a quantum superposition of several electron configurations of the \(5f\)-shell from \(f^3\) to, possibly, non-magnetic configuration \(f^0\). In this case, magnetic and charge fluctuations coexist in the antiferromagnetic state \[2\].

The authors will continue NMR studies at higher temperatures \(T > 375\) K in order to specify the dependence of the energy of spin fluctuations at a wider temperature range.
**Figure 3.** The temperature dependence of $(T_1)/TK$ for UN. The dashed and solid lines represent the results of approximation of the experimental data by a power function.

**Acknowledgements**

This work was supported by the Russian Science Foundation (project no. 18-72-10022). Magnetization measurements were carried out on the basis of ≪Test center of nanotechnology and advanced materials≫ of the M.N. Miheev Institute of Metal Physics of Ural Branch of the Russian academy of Sciences.

**References**

[1] Hill H H 1970 in: *Plutonium and Other Actinides* ed. by Miner W N (AIME, New York) p 2
[2] Ogloblichev V V, Potapov A M, Verkhovskii S V, Mirmelstein A V 2018 *JETP Letters* 108 616
[3] Staun Olsen J, Gerward L, Benedict U 1985 *J. Appl. Cryst.* 18 37
[4] Troč R 2006 *Pnictides and chalcogenides III (Actinide monopnictides)* edited by Wijn H P J, Landolt-Börnstein, New Series, Group III, Vol. 27 (Springer-Verlag, Berlin)
[5] Solontsov A Z, Silin V P 2004 *The Physics of Metals and Metallography* 97 35
[6] Samsel-Czekała M, Talik E, Du Plessis P de V, Troč R, Misiorek H, Sulkowski C 2007 *Physical Review B* 76 144426
[7] Chizhik V I, Chernyshev Y S, Donets A V, Frolov V, Komolkin A, Shelyapina M G 2014 *Magnetic Resonance and Its Applications* (Springer, Berlin)
[8] Piskunov Yu, Mikhailov K, Gerashenko A, Pogudin A, Ogloblichev V, Verkhovskii S, Tankeyev A, Arkhipov V, Zouev Yu, Lekomtsev S 2005 *Physical Review B* 71 174410
[9] O’Dell L A 2011 *Progress in Nuclear Magnetic Resonance Spectroscopy* 59 295
[10] Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Clarendon Press)
[11] Kuznietz M 1968 *J. Chem. Phys.* 49 3731
[12] Korringa J 1950 *Physica* 16 601
[13] Kuznietz M, Matzkanin G A 1969 *Physical Review* 178(2) 580
[14] Boutard J L, de Novion C H, Alloul H 1980 *Journal de Physique* 41 845
[15] Cox D L, Bickers N E, Wilkins J W 1985 *J. Appl. Phys.* 57 3166