JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 7, July 2008, p. 1663 - 1665

NMR investigation of quadrupole order parameter in actinide dioxides

Y. TOKUNAGA[a,*], Y. HOMMA[b], S. KAMBE[a], D. AOKI[b], H. SAKAI[a], H. CHUDO[a], K. IKUSHIMA[a,b], E. YAMAMOTO[a], A. NAKAMURA[a], Y. SHIOKAWA[b], R. E.WALSTEDT[a], H. YASUOKA[a]
[a]*Advanced Science Research Center, Japan Atomic Energy Research Institute, 2-4 Shirane, Tokai, Ibaraki 319-1195, Japan*
[b]*IMR Tohoku University, 2145-2 Narita Oarai Higashiibaraki Ibaraki 311-1313, Japan*

^{17}O-NMR have been performed to investigate the order parameters in actinide dioxides. In the antiferro-magnetic ordered state of UO_2, magnetic dipole and electric quadrupole order parameters have been extracted individually through the microscopic hyperfine interactions with ^{17}O nuclei. We have also detected the development of the quadrupole order parameter in the exotic multipolar ordering state of NpO_2. The large value of the critical exponent suggests the secondary character of the quadrupole ordering in NpO_2.

(Received April 1, 2008; accepted June 30, 2008)

Keywords: NMR, UO_2, NpO_2, Critical exponent1 Introduction

1. Introduction

Actinide dioxides (AnO_2: An = U, Np and Pu etc.) represent possibly the most intensely studied series of any actinide compounds. However, their surprisingly varied physical properties continue to be of interest. UO_2 exhibits an antiferro-magnetic (AFM) phase transition at T_N=30.8 K. The magnetic structure has been determined to be the *transverse* triple-**q** type, with an ordered moment of 1.74 μ_B/U atom [1-5]. This phase transition also causes an internal distortion of the oxygen cubes that surround the U cations [6,7]. Furthermore, the presence of an anisotropic 5f charge distribution at U site have been reported from ^{235}U NMR study [5]. Recent resonant x-ray scattering (RXS) measurements have confirmed the long-range nature of such 5f antiferro-quadrupolar (AFQ) ordering [8].

The low-temperature phase transition also appears at T_0=26K in NpO_2. The nature of this phase transition, however, has posed a challenge for both theory and experiment for half a century [9-13]. Recently, J.A.Paixão, *et al.*, have reported that the results of their RXS experiments are well accounted for assuming a triple-**q** longitudinal AFQ structure [14]. They proposed, further, that the AFQ order could be driven by the ordering of magnetic octupoles of Γ_5 symmetry. This Γ_5 antiferro-octupolar (AFO) ordered ground state has also been corroborated by recent microscopic calculations based on the *j-j* coupling scheme [15,16].

The quadrupolar ordering is triple-*q* in nature in both dioxides. The orientation of the electric quadrupoles is transverse in UO_2 [5,8], and longitudinal in NpO_2 [14,17]. In the previous work, we have reported that the quadrupole ordering is possible to detect by means of NMR through the hyperfine interaction with ^{17}O nuclei [18]. In this brief paper, we present a detailed analysis of the temperature dependence of the quadrupole order parameter in UO_2 and NpO_2. We shown that the large value of the critical exponent suggests a secondary character of the quadrupolar ordering in NpO_2.

2. Results and discussion

Fig. 1 (a) shows a temperature dependence of the internal field H_{int}, corresponding to the temperature dependence of the AFM order parameter in the ordered state of UO_2. The H_{int} is obtained from the width of ^{17}O-NMR spectrum forming a rectangular shape below T_N. The rectangular shape is a typical powder pattern spectrum in the AFM ordered state for the sites for which the internal field H_{int} is smaller than the applied external field H_{ext}[19]. The AFM order parameter appears discontinuously just below T_N, suggesting a 1st order-like phase transition in UO_2.

In Fig. 1(a), we also plot the recent RXS results [8]. In the RXS measurement, the integrated intensity I of the magnetic scattering is related to the square of the magnetization density. Hence, we plot the $I^{1/2}$ of the (112) reflection in $\sigma\rightarrow\pi$ polarization channel, which is also regarded to represent the development of the AFM order parameter. As seen in the figure, the NMR and RXS data follow a single curve below T_N. This confirms that both quantities reflect the same order parameter in UO_2.

Next we discuss the AFQ order parameter, which appears as a secondary effect of the AFM order. In the ordered state of UO_2, we have observed temperature

dependent oscillatory behavior on spin-echo decay $M(\tau)$. This spin-echo oscillation of $M(\tau)$ indicates the emergence of an axially symmetric electric field gradient (EFG) at O sites [20]. The electric quadrupole frequency ν_Q is then obtained from the oscillation frequency at each temperature. We show the temperature dependence of ν_Q in Fig. 1(b). A non-zero ν_Q rises up discontinuously just below T_N, and reaches a value ~9.3 kHz at low temperatures.

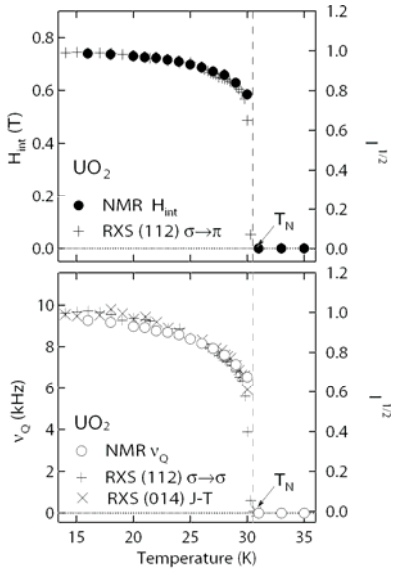

Fig. 1. The temperature dependence of (a) the internal field H_{int} and (b)the quadrupole frequency ν_Q obtained from ^{17}O-NMR in UO_2 [5]. These are plotted with the RXS data (see text) [8].

The temperature dependent EFG suggests the development of an anisotropic charge distribution associated with the secondary AFQ order below T_N. In addition to the electric contribution, however, a lattice contribution to the EFG is also important in the case of UO_2. Neutron experiments reported the oxygen displacement of 0.014 Å from their equilibrium position below T_N [6,7]. From the point charge calculation, the lattice contribution due to this oxygen displacement is estimated to be 3.0 kHz [5]. The value is still three times smaller than the experimental value of 9.3 kHz, which indicates the dominance of the electronic contribution to the EFG.

In Fig.1 (b), we also plot the RXS data. The $I^{1/2}$ of the (112) reflection in σ→σ polarization channel and the (014) Bragg reflection are regarded to represent the development of the AFQ order and the internal lattice distortion, respectively [8]. As seen in the figure, the NMR and RXS data agree on the temperature dependence with each other.

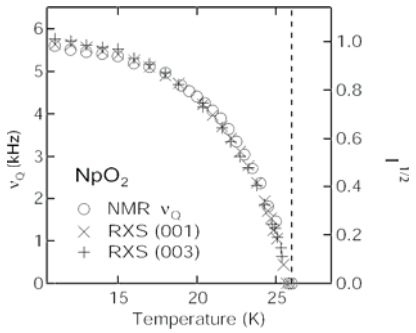

Fig. 2. The temperature dependence of NMR ν_Q in NpO_2 [18], plotted with the RXS data (see text) [22,23].

Next we turn to the multipolar ordered state of NpO_2. The development of the AFQ order parameter has been also observed in this ordered state [17,18]. Figure 2 shows the temperature dependence of ν_Q below T_0. The ν_Q values are obtained from the oscillation behavior of $M(\tau)$, in the same way as UO_2 [18]. A non-zero ν_Q rises up continuously below T_0 and reaches a value of ν_Q~5.7 kHz, which is smaller than the value of ν_Q ~9.3 kHz in UO_2.

In the case of NpO_2, the EFG is dominated by the electronic contribution, since the phase transition is not accompanied by any structural distortions [21,22]. From the angular dependence of oscillations (not shown), we have identified the principal axis of the EFG to be along the cubic crystal axes, which is in good accord with the longitudinal triple-**q** AFQ structure in NpO_2 [18].

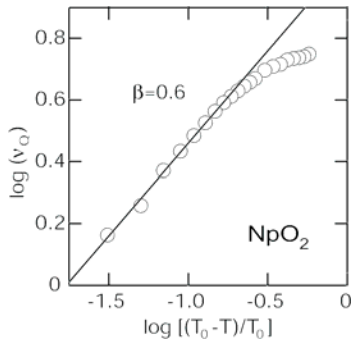

Fig. 3. The temperature dependence of ν_Q in NpO_2 with logarithmic scale. The solid line represents the curve with the critical exponent of β=0.6.

In the same figure, we also plot the $I^{1/2}$ of the (001) and (003) reflection reported from RXS measurements [22, 23]. These reflection were initially suggested to be of magnetic origin. However, they are now regarded as signaling the development of the AFQ order parameter. As shown in Fig. 2, the NMR and RXS data follow a single curve below T_0.

In Fig. 3, we plot the temperature dependence of ν_Q with logarithmic scale. The solid line represents the curve with the critical exponent of β=0.6. The value is much larger that the theoretical value of β~0.37 from the 3D

Heisenberg model characterized by a three-component order parameter and short-range interactions [24]. In terms of the ordinary Landau theory for a continuous phase transition, a secondary order parameter varies as the square of a primary order parameter and hence having the critical exponent of ~2β [25]. The large value of the critical exponent thus strongly suggests the secondary character of the AFQ order parameter in NpO_2 [23]. Since the AFM order is absent, the magnetic octupole is a likely candidate for the primary order parameter below T_0.

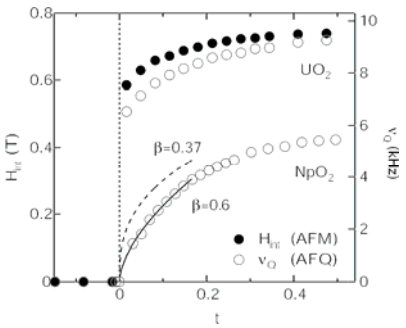

Fig. 4. Comparison of the magnetic and electric order parameters in actinide dioxides. Here the H_{int} and v_Q are plotted as a function of reduced temperature, i.e., $t=(T-T_N)T_N$ for UO_2 and $t=(T-T_0)T_0$ for NpO_2, respectively. The solid and dotted lines represent the curve with the critical exponent of β=0.6 (experiment) and 0.37 (3D Heisenberg model).

3. Summary

In summary, we compare the temperature dependence of the order parameters in UO_2 and NpO_2. In Fig.4, the NMR data are plotted as a function of reduced temperature. It is shown that the order parameter appears discontinuously in UO_2, while it rises up continuously in NpO_2. Furthermore, it is appeared that the development of the AFQ order parameter is rather gradual compared with the AFM order parameter in UO_2. This confirms that the AFQ order develops as a secondary effect of the primary AFM order. In NpO_2, on the other hand, magnetic order parameter has not been detected so far. However, the large value of the critical exponent suggests that the AFQ order appears as a secondary effect of the primary magnetic octupolar ordering in NpO_2.

Acknowledgment

The authors would like to thank K.Kubo, Hotta, O.Sakai and R.Shiina, for valuable discussions. This work was partly supported by a Grants-in-Aid for Young Scientists (B) from the Ministry of Education, Culture, Sports and Science and Technology of Japan.

References

[1] B. T. M. Willis, R. I. Taylor: Phys. Lett. **17** 188.
[2] G. Will, B. C. Frazer, G. Shirane, D. E. Cox, P. J. Brown : Phys. Rev. A **140**, 1448 (1965).
[3] P. Burlet, J. Rossat-Mignod, S. Vuevel, O. Vogt, J. C. Spirlet, J. Rebivant, J. Less-Common Met. **121** 121 (1986).
[4] G. Amoretti, A. Blaise, R. Caciuffo, J. M. Fournier, M. T. Hutchings, R. Osborn, A. D. Taylor : Phys. Rev. B **40,** 1856 (1989).
[5] K. Ikushima, S. Tsutsui, Y. Haga, H. Yasuoka, R. E. Walstedt, N. M. Masaki, A. Nakamura, S. Nasu, Y. Ōnuki: Phys. Rev. B **63,** 104404 (2001).
[6] J. Faber, G. H. Lander, B. R. Cooper: Phys. Rev. Lett. **35**, 1770 (1975).
[7] J. Faber, G. H. Lander: Phys. Rev. B **14**, 1151 (1976).
[8] S. B. Wilkins, R. Caciuffo, C. Detlefs, J. Rebizant, E. Colineau, F. Wastin, and G. H. Lander: Phys. Rev. B **73**, 060406(R) (2006).
[9] Darrel W. Osborne and Edgar F. Westrum, Jr., J. Chem. Phys. **21,** 1884 (1953).
[10] P Erdös and J. Robinson, The Physcs of Actinide Compounds (Plenum Press, New York, 1983)
[11] R. Caciuffo, G. H. Lander, J. C. Spirlet, J. M. Fournier, W. F. Kuhs, Solid State Commun. **64,** 149 (1987).
[12] J. M. Friedt, F. J. Litterst, J. Rebizant, Phys. Rev. B **32**, 257 (1985).
[13] P. Santini, G. Amoretti, Phys. Rev. Lett. **85**, 2188 (2000).
[14] J. A. Paixão, C. Detlefs, M. J. Longfield, R. Caciuffo, P. Santini, N. Bernhoeft, J. Rebizant, and G. H. Lander, Phys. Rev. Lett. **89**, 187202 (2002).
[15] K. Kubo, T. Hotta: Phys. Rev. B **71,** 140404(R) (2005).
[16] K. Kubo, T. Hotta: Phys. Rev. B **72,** 132411 (2005).
[17] M. Tokunaga, H. Song, Y. Tokunaga, and T. Tamegai: Phys. Rev. Lett. **94,** 137209 (2005).
[18] Y. Tokunaga, D. Aoki, Y. Homma, S. Kambe, H. Sakai, S. Ikeda, T. Fujimoto, R. E. Walstedt, H. Yasuoka, E. Yamamoto, A. Nakamura, Y. Shiokawa.: Phys. Rev. Lett. **97,** 257601 (2006).
[19] A. C. Gossard, J. P. Remeika, T. M. Rice, H. Yasuoka, Phys. Rev. B **9,** 1230 (1974).
[20] Hisashi Abe, Hiroshi Yasuoka, Akira Hirai, J. Phys. Soc. Jpn. **21,** 77 (1966).
[21] A. Boeuf, R. Caciuffo, J. M. Fournier, L. Manes, J. Rebizant, F. Rustichelli, J. C. Spirlet, A. Wright, Phys. Status Solidi A **79,** K1 (1983).
[22] D. Mannix, G. H. Lander, J. Rebizant, R. Caciuffo, N. Bernhoeft, E. Lidström, and C. Vettier : Phys. Rev. B **60,** 15187 (1999).
[23] R Caciuffo, J A Paixão, C Detlefs, M J Longfield, P Santini, N Bernhoeft, J Rebizant, G H Lander, J. Phys. Cond. Matt. **15**, S2287 (2003).
[24] Massimo Campostrini, Martin Hasenbusch, Andrea Pelissetto, Paolo Rossi, and Ettore Vicari: Phys. Rev. B **65,** 144520 (2002).
[25] M. B. Walker W. J. L. Buyers: Phys. Rev. Lett. **74,** 4097 (1995).

*Corresponding author: tokunaga@popsvr.tokai.jaeri.go.jp

JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 7, July 2008, p. 1663 - 1665