Letter

Resonant inelastic x-ray spectroscopy on UO₂ as a test case for actinide materials

G H Lander¹,², M Sundermann³,⁴, R Springell², A C Walters⁵, A Nag⁵, M Garcia-Fernandez⁵, K J Zhou⁵, G van der Laan⁵ and R Caciuffo¹,∗

¹ European Commission, Joint Research Centre (JRC), Postfach 2340, D-76125 Karlsruhe, Germany
² Interface Analysis Centre, School of Physics, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, United Kingdom
³ Institute of Physics II, University of Cologne, Zülpicher Straße 77, D-50937 Cologne, Germany
⁴ Max Planck Institute for Chemical Physics of Solids, Nöthnizer Straße 40, 01187 Dresden, Germany
⁵ Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, United Kingdom

E-mail: roberto.caciuffo@ec.europa.eu

Received 25 July 2020, revised 15 October 2020
Accepted for publication 26 October 2020
Published 11 November 2020

Abstract

Resonant inelastic x-ray spectroscopy at the uranium N₄ absorption edge at 778 eV has been used to reveal the excitations in UO₂ up to 1 eV. The earlier (1989) studies by neutron inelastic scattering of the crystal-field states within the 3H₄ multiplet are confirmed. In addition, the first excited state of the 3F₂ multiplet at ~520 meV has been established, and there is a weak signal corresponding to the next excited state at ~920 meV. This represents a successful application of soft x-ray spectroscopy to an actinide sample, and resolves an open question in UO₂ that has been discussed for 50 years. The technique is described and important caveats are drawn about possible future applications.

Keywords: RIXS, uranium dioxide, intermultiplet excitations, crystal field

(Some figures may appear in colour only in the online journal)

1. Introduction

The large 5f spin–orbit parameter in the actinides (ζ₅f ≈ 0.23 eV for uranium) implies that the appropriate many-electron interaction requires the intermediate coupling scheme, in which J is still a good quantum number, but L and S are not [1]. The Hamiltonian to describe the properties must contain, in addition to the spin–orbit coupling, the Slater integrals describing the Coulomb and exchange interactions. These interactions are normally scaled from their free-atom values by a Slater reduction factor g₅f due to the interactions in the solid. Finally, the crystal-field (CF) interaction must be included to account for the site symmetry of the actinide ion in the lattice and the electrostatic interactions with its neighbors. Depending on these parameters, the level structure of the actinide ion is stretched over several eV. These spectral features were first observed by optical absorption measurements and can be seen in the pioneering work of Carnall and Wybourne [2] on 5f³, and work on 5f² was reported later [3]. These optical techniques fail when the system is metallic, although they give a rough range for the excited states. In the U⁴⁺ (5f²) ionic uranium compounds, the ground state is a 3H₄ multiplet, and the excited states 3F₂ and 3H₅ are expected to lie at about 540–640 meV and 750–850 meV, respectively. In the U⁵⁺ case there is considerable mixing of L
Table 1. Comparison of calculated and experimental energies (in meV) of excited states up to ~1 eV in UO₂. The energy of the Γ₁ level given in parenthesis is a theoretical value, as the Γ₃ → Γ₁ transition has a vanishing intensity for inelastic neutron scattering. The values of the CF parameters V₄ and V₆ (in meV) are given for each model. For the reader’s convenience the irreducible representations of the CF levels are given in Bethe’s Γ notation as well as Mulliken notation (A₁, E, T₁₂).

| Multiplet | CF level | Theory | Optics | Neutrons | Raman | Theory | Theory | RIXS (this work) | Theory (this work) |
|-----------|----------|--------|--------|----------|--------|--------|--------|-----------------|------------------|
| V₄ (meV)  | −409     | −123   | −215   | −122     | −135   | −409   | −123   | −215            | −122             |
| g_{ff}    | 24.8     | 26.5   | 24.8   | 28.1     | 24.8   | 24.8   | 24.8   | 28.1            | 30               |
| g_{fc}    | 60% (5f−5f) | 60% (5d−5f) | 50% (5f−5f) | 80% (4d−5f) | 30     | 24.8   | 26.5   | 24.8            | 28.1             |

Table 1.

| Multiplet | Parameter values: |
|-----------|------------------|
| Γ₃(T₂)   | 0                 | 0                 | 0                 | 0                 | 0                 | 0                 | 0                 | 0                 |
| Γ₄(E)    | 170               | 230               | 150               | 0                 | 0                 | 0                 | 0                 | 0                 |
| Γ₄(T₁)   | 624               | 525               | 166               | 0                 | 0                 | 0                 | 0                 | 0                 |
| Γ₁(A₁)   | 710               | 630               | (175)             | 320               | 178               | 181               | 152               | ~150–200          |
| Γ₃(T₂)   | 809               | 765               | 512               | 764               | 652               | 512 ± 2           | 168               | ~150–200          |
| Γ₃(E)    | 918               | 850               | (175)             | 748               | 688               | 581 ± 2           | 178               | 205               |
| Γ₃(T₁)   | 727               | 720               | 715               | 643               | 870               | 512 ± 2           | 178               | 205               |
| Γ₃(E)    | 1183              | 1110              | 852               | 924               | 920               | 591               | 924               | ~920              |
| Γ₃(T₂)   | 1042              | 935               | 1072              | 938               | 1072              | 988               | 970               | 988               |
| Γ₃(T₁)   | 1274              | 1215              | 1108              | 970               | 970               | 988               | 988               | 988               |

and S values from intermediate coupling, so that a pure spectroscopic state becomes less meaningful. The J mixing is relatively small and the first excited states are J = 11/2 and J = 13/2 manifolds, respectively lying at about 500 and 940 meV above the 4I₀/₂ ground state. The range of values arises because of the CF splitting of the various ground states, and, of course, will vary for different compounds. In general, it is known that the CF interactions are larger for the ionic like compounds, since in metallic systems the screening by the conduction electrons reduces the CF potentials. The effective Coulomb and exchange interactions are also reduced in metallic systems.

The CF states are a unique fingerprint of the ground J state, and for metallic rare-earth materials neutron spectroscopy has been the tool of choice for the last 40 years [4]. Unfortunately, with some rare exceptions, such as UPd₃ [5], studies of metallic actinide systems with neutron scattering have a poor record of establishing the CF arrangement [6]. This is thought to be related to the strong hybridization of the 5f and conduction-band states, which washes out [7] the CF states so that they can no longer be observed. A relatively new technique of nonresonant inelastic x-ray scattering (NIXS) needs the detailed electronic structure to fit the x-ray data, so is a useful tool to understand the symmetry of the ground-state wave-functions, for example in URu₂Si₂ [8], and is also sensitive to the strength of the CF, as recently demonstrated in UO₂ [9]. However, none of these methods provide direct information of the excited-state levels.

At higher energies (up to ~1 eV) the technique of neutron scattering can observe intermultiplet transitions, and studies of the rare-earth metals, e.g. have been very successful [10, 11]. Efforts have been made on uranium systems UPd₃ [12], UPT₃ [12], and USb [13]. Later, problems of noise at high energies were found with one of the spectrometers at the ISIS neutron source [14]. However, the results for UPd₃ (but not UPT₃) were verified with a transition 3H₄ → 3F₂ at 395 meV. A similar transition was also found in URu₂Si₂ [15]. Experiments on systems with light elements (such as present in UO₂) are handicapped by the strong multiphonon background present at these higher energies and the small non-dipolar cross section for the 3H₄ → 3F₂ transition. Further experiments have not been reported in the last 20 years or so.

Recently, the technique of resonant inelastic x-ray scattering (RIXS) has been advanced to achieve resolutions of <50 meV, so it can be considered an additional technique to examine the actinides. Examples on Ce compounds [16, 17] have shown considerable promise up to energy transfers of ~0.5 eV, by using the Ce Ms absorption edge at 882 eV as incident energy, and with a resolution of 30 meV [17]. We present in this paper such experiments at the uranium N edge in uranium dioxide (UO₂).

UO₂ is probably the most studied of any actinide compound with extensive work going back to the 1960s. The first attempt to calculate the spectroscopic levels was by Rahman and Runciman [18] in 1966. This was followed by a study with optical techniques in 1980 [19]. In 1989 a neutron inelastic scattering experiment was able to unambiguously establish [20, 21] the CF transitions within the 3H₄ ground state, but could not observe the first excited multiplet state at higher energies. The CF parameters were confirmed by Nakotte et al using inelastic neutron scattering [22]. A Raman scattering investigation was reported by Livneh in 2008 [23]. In 2016 a new theoretical study was reported [24]. Recently, we completed a NIXS study of a single crystal of UO₂, and the values giving the best fit [9] to the observed spectra are listed, along with those from references [18–20, 24], in table 1.

There are considerable differences in these values in table 1, which is perhaps surprising considering the extent...
of our knowledge of UO₂ [25, 26], but illustrates the general uncertainty about the excited energy levels in all light actinide systems.

2. Experimental details and results

The UO₂ sample used was an atomically flat epitaxial film of thickness ~100 nm deposited on a substrate of yttrium-stabilised zirconia with the growth axis [001]. The sample mass was ~100 μg, which is almost six orders of magnitude smaller than the sample of 80 g used for the 1989 neutron experiments [20]. After fabrication of the sample in the sputtering chamber at the University of Bristol [27] it was transferred in a ‘vacuum suitcase’ to the Diamond Light Source. By using an interlock system, the sample was transferred into the vacuum chamber of beamline I21 [28] without any contact with air. At an incident x-ray energy of 778 eV (λ ≈ 16 Å) the 1/e attenuation length into UO₂ at an angle of incidence of ~20° is given by Henke et al [29] as 40 nm. However, these calculations do not take account of the strong white-line resonance at the N₄ absorption edge, common for soft x-ray energies [30], so the effective penetration is certainly far less than 20 nm, probably just a few nm, making this a surface sensitive experiment. This demand of a high-quality surface is a major disadvantage in the technique, and the role this plays in assessing the overall power of the technique is, as yet, challenging.

The RIXS experiment was performed by tuning to the uranium N₄ absorption peak (4d₁/₂ → 5f₅/₂ transition), which according to our calculation and experiment has a higher intensity than the N₅ peak. The resolution at this incident energy was 35 meV. The sample temperature was held at 15 K, i.e., below the transition temperature Tₘ of UO₂ [25]. The possible variation of the signal with temperature and with variation of the scattering vector (i.e., any dispersion) were only briefly examined, but no significant changes were observed. The results of the 16 h runs on the instrument are shown in figure 1. The spectra very clearly show the CF excitations peaked around 180 meV, the first excited multiplet of 3F₂ at 520–580 meV, and a weak signal at ~920 meV corresponding to the excited state multiplet of 3H₅.

3. Calculation

The N₄ edge RIXS is a photon-in photon-out process, 5fⁿ + hν₁ → 4d⁰ 5fⁿ⁺¹ → 5fⁿ + hν₂, in which an electron in the 4d3/2 core shell is promoted to the unoccupied 5f₅/₂ subshell of uranium, after which a 5f electron can decay back to the 4d core shell, so that it carries the spectral information of the 5f excited states.

For better interpretation of the spectra and extraction of the CF parameters, we performed a full-multiplet calculation using the Kramers–Heisenberg formulation with Quany [31], a simulation code that includes Coulomb and spin–orbit interactions. The calculation is based on a U⁴⁺ ion with two 5f electrons. In intermediate coupling the ground state is J = 4 in the cubic CF potential defined by the parameters V₄ and V₆, as described in reference [9]. The atomic parameters are calculated using Cowan’s atomic multiplet code [32] and the 5f–5f (4d–5f) Coulomb interactions are reduced to 50% (80%) to account for intra-atomic relaxation effects. Resonant spectra are calculated from a third order Green’s function [31]:

\[ G^{3}(ω₁,ω₂) = \langle χ|T^{1}_{ω₁} 1 1 \langle χ|T^{2}_{ω₂} 1 \langle χ|T^{1}_{ω₁} 1 \langle χ|T^{2}_{ω₂} 1 \langle χ|T^{1}_{ω₁} 1 \langle χ|T^{2}_{ω₂} \rangle \rangle \]

with T and H operators given in second quantization and ψᵢ being a many particle wavefunction. At the N edge, T₁ excite a 4d core electron into a 5f empty state and T₂ de-excite a 5f electron into the 4d core hole.

The Slater parameters for the initial and final states have been set to F² = 9.5 eV, F₄ = 6.2 eV, and F₆ = 4.6 eV. For the intermediate XAS state these values have been increased by about 5%. The atomic Coulomb interaction was reduced to 50% (80%) for 5f–5f (4d–5f). As shown in table 1, the obtained set of parameters shows good agreement with the neutron and NIXS study. The calculated spectra, shown by

Figure 1. RIXS spectra of UO₂ at the U N₄-edge (dots). Data were taken at 20° incident and 15° scattering angle with photon energy of 778 eV for linear horizontal π (top) and vertical σ polarization (bottom) as shown in the insets. The sample temperature was T = 15 K. The red lines show the calculated broadened RIXS spectrum for the U⁴⁺ 5f⁰ configuration for the CF parameters presented in table 1. The spectra recorded at the U N₅-edge in the energy transfer range 0.8–1.0 eV are shown in the inset of the upper panel (π-polarization channel). Spectra are calculated with a Lorentzian width of 5 meV (FWHM) and convoluted with a Gaussian of 30 meV (FWHM). The blue lines show the underlying multiplet peaks (with no line broadening) of the CF excitations around 180 meV and 3F₂ multiplet around 550 meV.
red lines in figure 1, reproduce well both the energies and the polarization dependencies of the experimental results. Note, that the splitting of the CF states in the $^3H_4$ and $^3F_2$ multiplets are related by the same parameters $V_4$ and $V_6$ hence limiting the quality of the fit.

4. Discussion

RIXS is described as consisting of two radiative transitions, absorption and emission, each one of which is regulated by the dipole-selection rules. The total RIXS transition, however, does not follow these rules. $ff$ excitations provide a typical example: the transition $5f → 5f$ would be forbidden by dipole, since $\Delta \ell = 0$, but the two steps $5d → 5f (\Delta \ell = +1)$ and $5f → 5d (\Delta \ell = -1)$ are allowed, making the whole transition possible. RIXS can therefore access transitions forbidden by dipole selection rules.

As each step follows the selection rules $\Delta J = 0, \pm 1$, the RIXS process allows also $\Delta J = \pm 2$. In fact, we observe a strong excitation for $\Delta J = 2$, for $^3H_4 → ^3F_2$ at $\sim 520 \text{ meV}$, but a weak one for $^3H_4 → ^3H_3$ at $\sim 920 \text{ meV}$ (a slightly stronger signal, shown in figure 1 inset, was observed at this position when the incident energy was tuned at the $N_3$ edge at $736 \text{ eV}$). This is exactly the opposite of the situation with neutrons, where the first excited level is non-dipolar, so is predicted to be weak [13, 14], and the second excitation should be stronger; however, energy transfers up to $1 \text{ eV}$ face difficulties due to the restrictions of the form factor in neutron studies [11]. The resonant process has no form factor, and x-rays are not subject to the kinematical restrictions present in neutron scattering due to the finite mass of the neutron. On the other hand, only the $^3H_4$ and $^3F_2$ multiplets are expected to yield a strong RIXS signal at the $N_4$ edge ($4d_{5/2}$), because only transitions into $5f_{5/2}$ are allowed, but not into $5f_{7/2}$. The other multiplets, however, do not necessarily give vanishing contributions to the spectra due to the Coulomb interaction. Experimentally, this is confirmed by the observation of the transition to the $^3H_4$ being stronger at the $N_4$ energy (see inset of figure 1) than at the $N_4$ shown in figure 1.

RIXS has also been shown to be very powerful in mapping dispersive excitations, especially of high-$T_c$ materials [33] and systems in which the dispersion relationships exceed $\sim 100 \text{ meV}$ [34]. Such studies are rare in the actinide systems, e.g. in UO$_2$ the magnetic excitations do not exceed $20 \text{ meV}$ [35], but in some systems, such as UFe$_2$ they may indeed continue to high energy [36].

We emphasize that this is an experimental paper showing how the technique of RIXS may allow further understanding of the electronic parameters in actinide systems. A more realistic model for UO$_2$ including configuration interaction would capture the electron–electron interactions to some extent and need less reduction of the $f→f$ Coulomb interactions. Such calculation (not shown) appears to differ at most by a larger energy splitting in the $^3F_2$ multiplet and explains the deviation we find with the ionic model. In table 1 we therefore also list the experimental peak positions, which have well separated $^3F_2$ states in the data. The results from the optical work of Schoenes [19] are difficult to assess because of the multi-phonon contributions. Although this reference claims the work supports the energies given by reference [18], it clearly does not. However, it does support (by the observation of a major line at $525 \text{ meV}$) later energy estimates of the $^3F_2$ excitation. The neutron work of reference [20] has a limited range ($<800 \text{ meV}$) of energy, but the values of the CF excitations are given in bold as they are reliable ($\pm 3 \text{ meV}$).

Two caveats should be stressed. (i) Success with UO$_2$ does not necessarily imply that the technique will work for metallic actinide compounds. The question of how the hybridization between the $5f$ states and those of the conduction electrons affects the observation of $f→f$ excitations is not yet answered for the actinides. Indeed, in recent experiments (at the same beamline) on a localized system UNi$_2$Si$_2$ [37] no excitations were observed. The RIXS technique does work for Ce metallic systems [16, 17], but the hybridization of the $5f$ states is more complicated than that of the $4f$ states in cerium. There are also difficulties in observing CF transitions in actinide intermetallic systems [7] with neutron scattering. (ii) The RIXS technique is exceedingly surface sensitive, probably at the level of a few nm, so that excessive care has to be taken in sample preparation. The UO$_2$ sample used here was atomically flat and was never exposed to air. Whether such care has to be taken for the technique to be successful remains an open question.

5. Conclusions

Our experiments have elucidated the higher $5f$ related excitations in UO$_2$ that have been a source of speculation for at least 50 years. The use of soft x-ray spectroscopy (RIXS) thus opens up the actinides to such studies, in the same way that it has allowed studies of cerium compounds [16, 17], and the observation of dispersion at high-energy transfers in transition-metal systems [33, 34]. The technique has confirmed the neutron experiments on the CF levels on UO$_2$ performed 30 years ago [20], and extends that study to clearly show the $f→f$ level structure up to $1 \text{ eV}$, which is difficult with neutron scattering. The reported excitations in UPd$_3$ (at $395 \text{ meV}$) [14] and URu$_2$Si$_2$ (at $363 \text{ meV}$) [15] still remain to be understood. The $\sim 25\%$ reduction of these excitations from UO$_2$ seems a very large amount. Further experiments and theory will be needed to understand these differences, and their significance to fundamental parameters describing materials with $5f$ electrons.

Acknowledgments

The RIXS experiments were carried out on beamline I21 at the Diamond Light Source, UK, under proposal MM24583. We thank Andrea Severing and Andrea Amorose for discussions and sharing some of their results on RIXS from Diamond Light Source, and also Keith McEwen for discussions on the neutron scattering studies. MS gratefully acknowledges the financial support of the Deutsche Forschungsgemeinschaft under project SE1441-5-1.
References

[1] Moore K T and van der Laan G 2009 Rev. Mod. Phys. 81 235
[2] Carnall W T and Wybourne B G 1964 J. Chem. Phys. 40 3428
[3] Carnall W T, Liu G K, Williams C W and Reid M F 1991 J. Chem. Phys. 95 7194
[4] Fulde P and Loewenhaupt M 1985 Adv. Phys. 34 589
[5] Le M D, McEwen K A, Rotter M, Doerr M, Barcza A, Park J-G, Brooks J, Jobiliong E and Fort D 2014 Phys. Rev. B 89 235114
[6] Edelstein N M and Lander G H 2006 Magnetic studies of transplutonium actinides The Chemistry of the Actinide and Transactinide Elements ed L M Morss, N M Edelstein and J Fuger (Berlin: Springer) ch 20 p 2225
[7] Hu G-J and Cooper B R 1993 Phys. Rev. B 48 12743
[8] Sundermann M et al 2016 Proc. Natl Acad. Sci. USA 113 13989
[9] Sundermann M, van der Laan G, McEwen K A, Goremychkin E A and Taylor A D 1990 Phys. B 163 37
[10] Jones D L, Stirling W G, Lander G H, Osborn R, Taylor A D, Mattenberger K and Vogt O 1992 Phys. B 180-181 199
[11] Bull M J, McEwen K A, Osborn R and Eccleton S 1996 Phys. B 223-224 175
[12] Park J-G, McEwen K A and Bull M J 2002 Phys. Rev. B 66 094502
[13] Amorese A et al 2016 Phys. Rev. B 93 165134
[14] Amorese A et al 2018 Phys. Rev. B 98 081116(R)
[15] Rahman H U and Runciman W A 1966 J. Phys. Chem. Solids 27 1833
[16] Schoenes J 1980 Phys. Rep. 63 301
[17] Amoretti G, Blaise A, Caciuffo R, Fournier J M, Hutchings M T, Osborn R and Taylor A D 1989 Phys. Rev. B 40 1856–70
[18] Magnani N, Santini P, Amoretti G and Caciuffo R 2005 Phys. Rev. B 71 054405
[19] Nakotte H, Rajaram R, Kern S, McQueeney R J, Lander G H and Robinson R A 2010 J. Phys.: Conf. Ser. 251 012002
[20] Livneh T 2008 J. Phys.: Condens. Matter 20 085202
[21] Ramanantoanina H, Kuri G, Daul C and Bertsch J 2016 Phys. Chem. Chem. Phys. 18 19020
[22] Santini P, Carretta S, Amoretti G, Caciuffo R, Magnani N and Lander G H 2009 Rev. Mod. Phys. 81 807
[23] Lander G H and Caciuffo R 2020 J. Phys.: Condens. Matter 32 374001
[24] Rennie S, Lawrence Bright E, Dambrough J E, Paolasini L, Bosak A, Smith A D, Mason N, Lander G H and Springell R 2018 Phys. Rev. B 97 224303
[25] K J Zhou 2020 I21: resonant inelastic x-ray scattering https://diamond.ac.uk/Instruments/Magnetic-Materials/I21.html
[26] Henke B L, Gullikson E M and Davis J C 1993 X-ray interactions with matter http://henke.lbl.gov/optical_constants/
[27] Cross J O, Newville M, Rehr J J, Sorensen L B, Boulid C E, Watson G, Gouder T, Lander G H and Bell M I 1998 Phys. Rev. B 58 11215
[28] Chaix L et al 2017 Nat. Phys. 13 952–6
[29] Fabbris G et al 2017 Phys. Rev. Lett. 118 156402
[30] Caciuffo R, Santini P, Carretta S, Amoretti G, Hiess A, Magnani N, Regnault L-P and Lander G H 2011 Phys. Rev. B 84 104409
[31] Paolissi L, Lander G H, Shapiro S M, Caciuffo R, Lebech B, Regnault L-P, Roesli B and Fournier J-M 1996 Phys. Rev. B 54 7222
[32] Amorese A et al 2020 Dual nature of 5f electrons in the isostructural UM3Si2 family: from antiferro- to pauli paramagnetism via hidden order (arXiv:2004.13419)