

ACCEPTED MANUSCRIPT • OPEN ACCESS

Resonant inelastic x-ray spectroscopy on UO_2 as a test case for actinide materials

To cite this article before publication: G H Lander *et al* 2020 *J. Phys.: Condens. Matter* in press <https://doi.org/10.1088/1361-648X/abc4d2>

Manuscript version: Accepted Manuscript

Accepted Manuscript is “the version of the article accepted for publication including all changes made as a result of the peer review process, and which may also include the addition to the article by IOP Publishing of a header, an article ID, a cover sheet and/or an ‘Accepted Manuscript’ watermark, but excluding any other editing, typesetting or other changes made by IOP Publishing and/or its licensors”

This Accepted Manuscript is © 2020 The Author(s). Published by IOP Publishing Ltd..

As the Version of Record of this article is going to be / has been published on a gold open access basis under a CC BY 3.0 licence, this Accepted Manuscript is available for reuse under a CC BY 3.0 licence immediately.

Everyone is permitted to use all or part of the original content in this article, provided that they adhere to all the terms of the licence <https://creativecommons.org/licenses/by/3.0>

Although reasonable endeavours have been taken to obtain all necessary permissions from third parties to include their copyrighted content within this article, their full citation and copyright line may not be present in this Accepted Manuscript version. Before using any content from this article, please refer to the Version of Record on IOPscience once published for full citation and copyright details, as permissions may be required. All third party content is fully copyright protected and is not published on a gold open access basis under a CC BY licence, unless that is specifically stated in the figure caption in the Version of Record.

View the [article online](#) for updates and enhancements.

Resonant inelastic x-ray spectroscopy on UO_2 as a test case for actinide materials

G. H. Lander,^{1,2} M. Sundermann,^{3,4} R. Springell,² A. C. Walters,⁵ A. Nag,⁵
M. Garcia-Fernandez,⁵ K. J. Zhou,⁵ G. van der Laan,⁵ and R. Caciuffo¹

¹European Commission, Joint Research Centre (JRC), Postfach 2340, D-76125 Karlsruhe, Germany

²Interface Analysis Centre, School of Physics, University of Bristol,
Tyndall Avenue, Bristol, BS8 1TL, United Kingdom

³Institute of Physics II, University of Cologne, Zùlpicher StraÙe 77, D-50937 Cologne, Germany

⁴Max-Planck-Institute for Chemical Physics of Solids - Nöthnizer StraÙe 40, 01187 Dresden, Germany

⁵Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, UK

(Dated: October 15, 2020)

Resonant inelastic x-ray spectroscopy at the uranium N_4 absorption edge at 778 eV has been used to reveal the excitations in UO_2 up to 1 eV. The earlier (1989) studies by neutron inelastic scattering of the crystal-field states within the 3H_4 multiplet are confirmed. In addition, the first excited state of the 3F_2 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 UO_2 that has been discussed for 50 years. The technique is described and important caveats are drawn about possible future applications.

I. INTRODUCTION

The large $5f$ spin-orbit parameter in the actinides ($\zeta_{5f} \approx 0.23$ 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 g_{ff} 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 $5f^3$, and work on $5f^2$ 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 U^{4+} ($5f^2$) ionic uranium compounds, the ground state is a 3H_4 multiplet, and the excited states 3F_2 and 3H_5 are expected to lie at about 540-640 meV and 750-850 meV, respectively. In the U^{3+} ($5f^3$) case there is considerable mixing of L 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 $^4I_{9/2}$ 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 UPd_3 [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 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 URu_2Si_2 [8], and is also sensitive to the strength of the CF, as recently demonstrated in UO_2 [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 (IMT), and studies of the rare-earth metals, *e.g.* have been very successful [10, 11]. Efforts have been made on uranium systems UPd_3 [12], UPT_3 [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 UPd_3 (but not UPT_3) were verified with a transition $^3H_4 \rightarrow ^3F_2$ at 395 meV. A similar transition was also found in URu_2Si_2 [15]. Experiments on systems with light elements (such as present in UO_2) are handicapped by the strong multiphonon background present at these higher energies and the small non-dipolar cross section for the $^3H_4 \rightarrow ^3F_2$ 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 tech-

nique 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 M_5 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 (UO_2).

UO_2 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 3H_4 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 UO_2 , and the values giving the best fit [9] to the observed spectra are listed, along with those from Refs. [18–20, and 24] in Table I.

There are considerable differences in these values in Table I, which is perhaps surprising considering the extent of our knowledge of UO_2 [25, 26], but illustrates the general uncertainty about the excited energy levels in all light actinide systems.

II. EXPERIMENTAL DETAILS AND RESULTS

The UO_2 sample used was an atomically flat epitaxial film of thickness ~ 100 nm deposited on a substrate of yttrium-stabilised zirconia (YSZ) 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 ($\lambda \approx 16$ Å) the $1/e$ attenuation length into UO_2 at an angle of incidence of $\sim 20^\circ$ 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 N_4 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 N_4 absorption peak ($4d_{3/2} \rightarrow 5f_{5/2}$ transition), which according to our calculation and experiment has

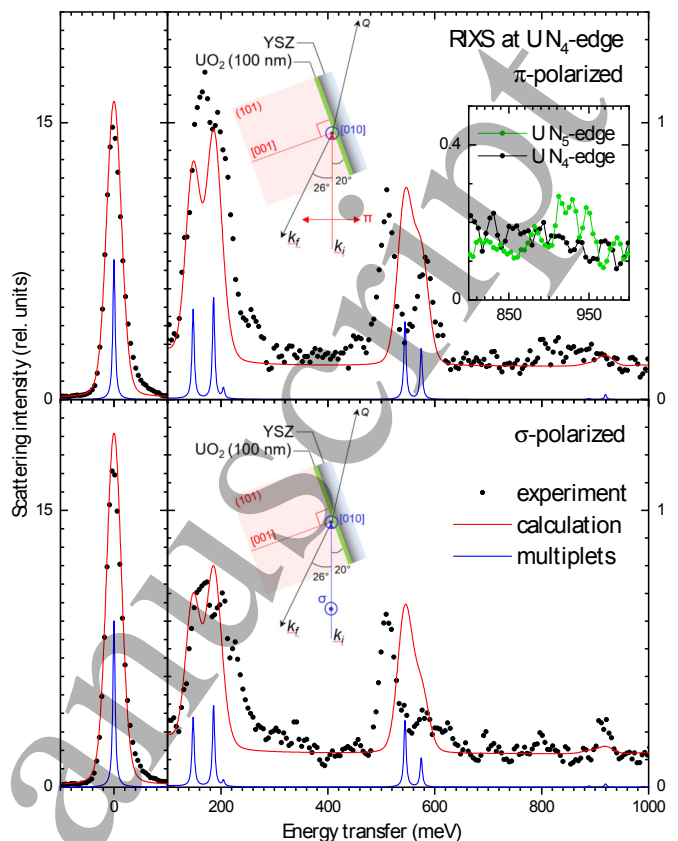


FIG. 1. (Color online). RIXS spectra of UO_2 at the U N_4 -edge (dots). Data were taken at 20° incident and 154° scattering angle with photon energy of 778 eV for linear horizontal π (top) and vertical σ polarization (bottom) as shown in the insets. The sample temperature was $T = 15$ K. The red lines show the calculated broadened RIXS spectrum for the $\text{U}^{4+} 5f^2$ configuration for the CF parameters presented in Table I. The spectra recorded at the U N_5 -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 3F_2 multiplet around 550 meV.

a higher intensity than the N_5 peak. The resolution at this incident energy was 35 meV. The sample temperature was held at 15 K, i.e., below the transition temperature T_N of UO_2 [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-hr runs on the instrument are shown in Fig. 1. The spectra very clearly show the CF excitations peaked around 180 meV, the first excited multiplet of 3F_2 at 520–580 meV, and a weak signal at ~ 920 meV corresponding to the excited state multiplet of 3H_5 .

III. CALCULATIONS

The N_4 edge RIXS is a photon-in photon-out process, $5f^n + h\nu_1 \rightarrow 4d^9 5f^{n+1} \rightarrow 5f^{n*} + h\nu_2$, in which an electron in the $4d_{3/2}$ core shell is promoted to the unoccupied $5f_{5/2}$ 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 **Quanty** [31], a simulation code that includes Coulomb and spin-orbit interactions. The calculation is based on a U^{4+} ion with two $5f$ electrons. In intermediate coupling the ground state is $J = 4$ in the cubic CF potential defined by the parameters V_4 and V_6 , as described in Ref. [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]:

$$G^3(\omega_1, \omega_2) = \langle \chi_i | T_1^\dagger \frac{1}{\omega_1 - H_1 - i\Gamma/2} T_2^\dagger \frac{1}{\omega_2 - H_2 + i\Gamma/2} T_2 \frac{1}{\omega_1 - H_1 + i\Gamma/2} T_1 | \chi_i \rangle \quad (1)$$

with T and H operators given in second quantization and ψ_i being a many particle wavefunction. At the N edge, T_1 excite a $4d$ core electron into a $5f$ empty state and T_2 de-excite a $5f$ electron into the $4d$ core hole.

The Slater parameters for the initial and final states have been set to $F^2 = 9.5$ eV, $F^4 = 6.2$ eV, and $F^6 = 4.6$ 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 I, the obtained set of parameters shows good agreement with the neutron and NIXS study. The calculated spectra, shown by red lines in Fig. 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.

IV. 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 $5f \rightarrow 5f$ would be forbidden by dipole, since $\Delta\ell = 0$, but the two steps $5d \rightarrow 5f$ ($\Delta\ell = +1$) and $5f \rightarrow 5d$ ($\Delta\ell = -1$) 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 ${}^3H_4 \rightarrow {}^3F_2$ at ~ 520 meV, but a weak one for ${}^3H_4 \rightarrow {}^3H_5$ at ~ 920 meV (a slightly stronger signal, shown in Fig. 1 inset, was observed at this position when the incident energy was tuned at the N_5 edge at 736 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 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 ($4d_{3/2}$), 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_5 being stronger at the N_5 energy (see inset of Fig. 1) than at the N_4 shown in Fig. 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 ~ 100 meV [34]. Such studies are rare in the actinide systems, e.g. in UO_2 the magnetic excitations do not exceed 20 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 $5f$ - $5f$ 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 I 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 multiphonon contributions. Although this reference claims the work supports the energies given by Ref. [18], it clearly does not. However, it does support (by the observation of a major line at 525 meV) later energy estimates of the 3F_2 excitation. The neutron work of Ref. [20] has a limited range (< 800 meV) of energy, but the values of the CF excitations are given in bold as they are reliable (± 3 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

TABLE I. Comparison of calculated and experimental energies (in meV) of excited states up to ~ 1 eV in UO_2 . The energy of the Γ_1 level given in parenthesis is a theoretical value, as the $\Gamma_5 \rightarrow \Gamma_1$ transition has a vanishing intensity for inelastic neutron scattering. The values of the CF parameters V_4 and V_6 (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 ($A_1, E, T_{1,2}$).

Multiplet	CF level	Theory [18]	Optics [19]	Neutrons [20]	Raman [23]	Theory [24]	Theory [9]	RIXS [this work]	Theory [this work]
Parameter	V_4 (meV)	-409		-123		-215	-122		-135
values:	V_6 (meV)	24.8		26.5		24.8	28.1		30
	g_{ff}						60% ($5f-5f$)		50% ($5f-5f$)
	g_{fc}						60% ($5d-5f$)		80% ($4d-5f$)
3H_4	Γ_5 (T_2)	0	0	0	0	0	0	0	0
	Γ_3 (E)	170	230	150		181	152	$\sim 150-200$	148
	Γ_4 (T_1)	624	525	166		271	168	$\sim 150-200$	186
3F_2	Γ_1 (A_1)	710	630	(175)		320	178		205
	Γ_5 (T_2)	809	765		512	764	652	512 ± 2	544
3H_5	Γ_3 (E)	918	850		548	748	688	581 ± 2	575
	Γ_4 (T_1)	727	720		715	643	870		888
	Γ_3 (E)	1183	1110			852	924	~ 920	919
	Γ_5 (T_2)	1042	935			938	1072		1062
	Γ_4 (T_1)	1274	1215			1108	970		988

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_2Si_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.

V. 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 crystal-field levels on UO_2 performed 30 years ago [20], and extends that study to clearly show the $f-f$ level structure up to 1 eV, which is difficult with neutron scattering. The reported excitations in UPd_3 (at 395 meV) [14] and URu_2Si_2 (at 363 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.

VI. ACKNOWLEDGMENT

The RIXS experiments were carried out on beamline I21 at the Diamond Light Source, UK, under proposal MM24583. We thank Andrea Severing and Andrea Amorese 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. M.S. gratefully acknowledges the financial support of the Deutsche Forschungsgemeinschaft under project SE1441-5-1.

- [1] K. T. Moore and G. van der Laan, *Rev. Mod. Phys.* **81**, 235 (2009).
 [2] W. T. Carnall and B. G. Wybourne, *J. Chem. Phys.* **40**, 3428 (1964).
 [3] W. T. Carnall, G. K. Liu, C. W. Williams, and M. F. Reid, *J. Chem. Phys.* **95**, 7194 (1991).
 [4] P. Fulde and M. Loewenhaupt, *Adv. Phys.* **34**, 589 (1985).

- [5] M. D. Le, K. A. McEwen, M. Rotter, M. Doerr, A. Barcza, J.-G. Park, J. Brooks, E. Jobilong, and D. Fort, *Phys. Rev. B* **89**, 235114 (2014).
 [6] N. M. Edelstein and G. H. Lander, *Magnetic studies of transplutonium actinides*, in *The Chemistry of the actinide and Transactinide elements. Ch. 20*, edited by L. M. Morss, N. M. Edelstein, and J. Fuger (Springer, 2006) p. 2225.

- [7] G. J. Hu and B. R. Cooper, *Phys. Rev. B* **48**, 12743 (1993).
- [8] M. Sundermann, M. W. Haverkort, S. Agrestini, A. Al-Zein, M. Moretti Sala, Y. Huang, M. Golden, A. de Visser, P. Thalmeier, L. H. Tjeng, and A. Severing, *Proc. Nat. Acad. Science U.S.A.* **113**, 13989 (2016).
- [9] M. Sundermann, G. van der Laan, A. Severing, L. Simonelli, G. H. Lander, M. W. Haverkort, and R. Caciuffo, *Phys. Rev. B* **98**, 205108 (2018).
- [10] A. D. Taylor, R. Osborn, K. A. McEwen, W. G. Stirling, Z. A. Bowden, W. G. Williams, E. Balcar, and S. W. Lovesey, *Phys. Rev. Lett.* **61**, 1309 (1988).
- [11] R. Osborn, S. W. Lovesey, A. D. Taylor, and E. Balcar, in *Handbook on the Physics and Chemistry of Rare Earths. Vol. 14*, edited by K. Gschneidner and L. Eyring (Elsevier Science Publishers (Amsterdam), 1991) p. Ch. 23.
- [12] R. Osborn, K. A. McEwen, E. A. Goremychkin, and A. D. Taylor, *Physica B* **163**, 37 (1990).
- [13] D. L. Jones, W. G. Stirling, G. H. Lander, R. Osborn, A. D. Taylor, K. Mattenberger, and O. Vogt, *Physica B* **180-181**, 199 (1992).
- [14] M. J. Bull, K. A. McEwen, R. Osborn, and R. S. Eccleston, *Physica B* **223-224**, 175 (1996).
- [15] J.-G. Park, K. A. McEwen, and M. J. Bull, *Phys. Rev. B* **66**, 094502 (2002).
- [16] A. Amorese, G. Dellea, M. Fanciulli, S. Seiro, C. Geibel, C. Krellner, I. P. Makarova, L. Braicovich, G. Ghiringhelli, D. V. Vyalikh, N. B. Brookes, and K. Kummer, *Phys. Rev. B* **93**, 165134 (2016).
- [17] A. Amorese, K. Kummer, N. B. Brookes, O. Stockert, D. T. Adroja, A. M. Strydom, A. Sidorenko, H. Winkler, D. A. Zocco, A. Prokofiev, S. Paschen, M. W. Haverkort, L. H. Tjeng, and A. Severing, *Phys. Rev. B* **98**, 081116(R) (2018).
- [18] H. U. Rahman and W. A. Runciman, *J. Phys. Chem. Solids* **27**, 1833 (1966).
- [19] J. Schoenes, *Physics Reports* **63**, 301 (1980).
- [20] G. Amoretti, A. Blaise, R. Caciuffo, J. M. Fournier, M. T. Hutchings, R. Osborn, and A. D. Taylor, *Phys. Rev. B* **40**, 1856 (1989).
- [21] N. Magnani, P. Santini, G. Amoretti, and R. Caciuffo, *Phys. Rev. B* **71**, 054405 (2005).
- [22] H. Nakotte, R. Rajaram, S. Kern, R. J. McQueeney, G. H. Lander, and R. A. Robinson, *J. Phys.: Conf. Series* **251**, 012002 (2010).
- [23] T. Livneh, *J. Phys.: Cond. Matter* **20**, 085202 (2008).
- [24] H. Ramanantoanina, G. Kuri, C. Daul, and J. Bertsch, *Phys. Chem. Chem. Phys.* **18**, 19020 (2016).
- [25] P. Santini, S. Carretta, G. Amoretti, R. Caciuffo, N. Magnani, and G. H. Lander, *Rev. Mod. Phys.* **81**, 807 (2009).
- [26] G. H. Lander and R. Caciuffo, *J. Phys.: Cond. Matter* **32**, 374001 (2020).
- [27] S. Rennie, E. Lawrence Bright, J. E. Darnbrough, L. Paolasini, A. Bosak, A. D. Smith, N. Mason, G. H. Lander, and R. Springell, *Phys. Rev. B* **97**, 224303 (2018).
- [28] I21: Resonant inelastic x-ray scattering, <https://www.diamond.ac.uk/Instruments/Magnetic-Materials/I21.html>.
- [29] B. Henke, E. Gullikson, and J. Davis, X-ray interactions with matter, http://henke.lbl.gov/optical_constants/.
- [30] J. O. Cross, M. Newville, J. J. Rehr, L. B. Sorensen, C. E. Bouldin, G. Watson, T. Gouder, G. H. Lander, and M. I. Bell, *Phys. Rev. B* **58**, 11215 (1998).
- [31] M. W. Haverkort, *J. Phys.: Conf. Ser.* **712**, 012001 (2016).
- [32] R. Cowan, *The theory of atomic structure and spectra*, University of California, Berkley (1981).
- [33] L. Chaix, G. Ghiringhelli, Y. Y. Peng, M. Hasegawa, B. Moritz, K. Kummer, N. B. Brookes, Y. He, S. Chen, S. Ishida, Y. Yosida, H. Eisaki, M. Salluzzo, L. Braicovich, Z. X. Shen, T. P. Devereaux, and W. S. Lee, *Nature Phys.* **13**, 952-956 (2017).
- [34] G. Fabbris, D. Meyers, L. Xu, V. M. Katukuri, L. Hozoi, X. Liu, Z.-Y. Chen, J. Okamoto, T. Schmitt, A. Uldry, B. Delley, G. D. Gu, D. Prabhakaran, A. T. Boothroyd, J. van den Brink, D. J. Huang, and M. P. M. Dean, *Phys. Rev. Lett.* **118**, 156402 (2017).
- [35] R. Caciuffo, P. Santini, S. Carretta, G. Amoretti, A. Hiess, N. Magnani, L.-P. Regnault, and G. H. Lander, *Phys. Rev. B* **84**, 104409 (2011).
- [36] L. Paolasini, G. H. Lander, S. M. Shapiro, R. Caciuffo, B. Lebeck, L.-P. Regnault, B. Roessli, and J.-M. Fournier, *Phys. Rev. B* **54**, 7222 (1996).
- [37] A. Amorese, M. Sundermann, B. Lebeck, A. Marino, D. Takegami, H. Gretarsson, A. Gloskovskii, C. Schlüter, M. W. Haverkort, Y. Huang, M. Szwalska, D. Kaczorowski, R. Sheng, M. B. Maple, E. D. Bauer, A. Leithe-Jasper, P. Thalmeier, L. H. Tjeng, and A. Severing, Dual nature of $5f$ electrons in the isostructural um_2si_2 family: from antiferro- to pauli paramagnetism via hidden order, arXiv:2004.13419 (2020).