# X-ray spectroscopies on 4*f* and 5*f* systems

*Andrea Severing[#], Andrea Amorese, Andrea Marino, Martin Sundermann, Peter Thalmeier, and Liu Hao Tjeng[##]*

**Heavy-fermion compounds are fascinating materials that raise fundamental questions in the field of strongly correlated matter. Their physical properties are driven by the hybridization of the atomic-like *f* electrons with those of the conduction band (*cf*-hybridization). Unconventional superconductivity, Kondo insulating behavior together with putative strongly correlated topology, hidden order, or the dual nature of the 5*f* electrons in uranium compounds are some of the intriguing phenomena to be investigated. The group applies state-of-the-art synchrotron-based methods such as x-ray absorption (XAS), non-resonant inelastic x-ray scattering (NIXS) in the beyond dipole limit, resonant inelastic x-ray scattering (RIXS), and hard x-ray photoelectron spectroscopy (HAXPES) to investigate the symmetry of the ground state, the low energy excitations, as well as the itinerant aspects of the entangled ground state. All data analysis is performed with atomic full multiplet codes, either XTLS by A. Tanaka or Quanty by M. W. Haverkort.**

### Symmetry and orientation of 4*f* ground state orbital in Ce*M*In$_5$ [1, 2]

The heavy fermion Ce*M*In$_5$ family with *M*=Co, Rh, Ir exhibits ambient pressure superconductivity (Co, Ir) and antiferromagnetic order (Rh). Here the question arises why some members of the family are superconductors while others exhibit an antiferromagnetic ground state. Our investigation of the substitution series $CeRh_{1-\delta}Ir_{\delta}In_5$ revealed a correlation of the ground state orbital with the phase diagram: the 4*f* orbitals of superconducting $CeCoIn_5$, $CeIrIn_5$, and Ir-rich $CeRh_{1-\delta}Ir_{\delta}In_5$ are more elongated in the *c*-direction in comparison to those of the anti-ferromagnetic members of the $CeRh_{1-\delta}Ir_{\delta}In_5$ series [3]. The enhanced hybridization of Ce with out-of-plane In2 ions (see Fig. 1) provides a natural explanation why the taller orbitals favor superconductivity.

The investigation of the ground state wave function of the heavy fermion substitution series $CeCoIn_5$ upon Cd and Sn substitution on the In site [1] is a follow up study of the above mentioned study of $CeRh_{1-\delta}Ir_{\delta}In_5$. Lattice effects due to substitution with Sn or Cd are minor but the electron doping (Sn) or hole doping (Cd) has very different consequences on the *cf* hybridization. Only a few percent of Cd suppress the superconducting ground state and antiferromagnetic order forms. Sn substitution, on the other hand, suppresses superconductivity and leads to a more strongly hybridized ground state according to electrical resistivity measurements. Our investigation of $CeCo(In_{1-x}Cd_x)_5$ and $CeCo(In_{1-y}Sn_y)_5$ with linear polarized XAS at the ID32 beamline at ESRF in Grenoble showed an increasing extension of the 4*f* orbitals in the tetragonal *ab*-plane of the Sn doped samples, in agreement with XAFS findings that the Sn ions go favorably to the in-plane In1 sites (see Fig. 1). Hence, this study establishes that the 4*f* wave functions are a very sensitive probe for small changes of *cf*-hybridization, even conveying information about directional dependencies.

Non-resonant inelastic x-ray scattering (NIXS) was applied to $CeCoIn_5$ and $CeRhIn_5$ after we had shown the potential of this technique at the examples of $CeCu_2Si_2$ and $CeB_6$ [4, 5]. Crystal-field energies and parameters of the Ce115 compounds had been determined in great detail in the past but whether the ground state wave function is a $\Gamma_7^- = \alpha|\pm\frac{5}{2}\rangle - \sqrt{1-\alpha^2}|\mp\frac{3}{2}\rangle$ with xy orientation or the $\Gamma_7^+ = \sqrt{1-\alpha^2}|\pm\frac{5}{2}\rangle + \alpha^2|\mp\frac{3}{2}\rangle$ with $x^2$-$y^2$ orientation remained undetermined (see Fig. 1). Its knowledge, however, is relevant for understanding which hybridization channels are the leading ones, via the out-of-plane In2 or the in-plane In1, or both.

Dipole methods like inelastic neutron scattering or XAS are insensitive to anisotropies within the tetragonal *ab* plane. We, therefore, applied NIXS. The NIXS signal at the Ce $N_{4,5}$ edges, when measured with large momentum transfers, contains scattering contributions that are due to higher-than-dipole transitions. NIXS is then sensitive to the orbital orientation in the tetragonal *ab* plane [4, 5]. The

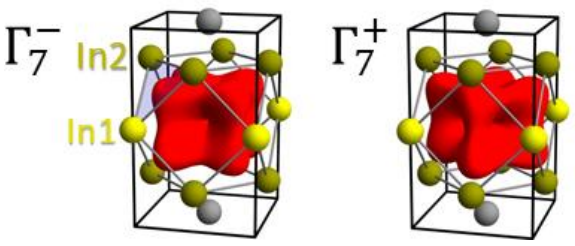


*Fig. 1: $\Gamma_7^{-/+}$ $\Gamma_7$ orbitals in unit cell of CeMIn$_5$; In1 yellow, In2 dark yellow, transition metal grey, and Ce red.*

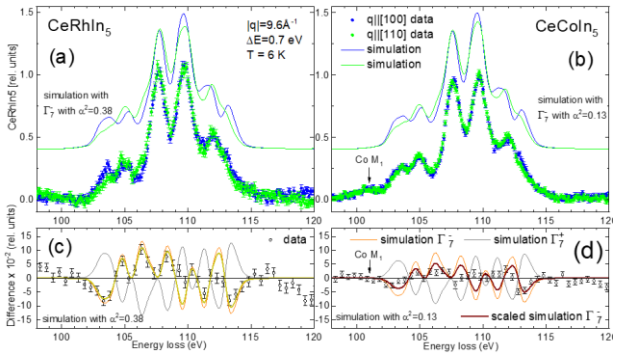


*Fig. 2: a) and b) NIXS data (dots) of $CeRhIn_5$ and $CeCoIn_5$ for two directions of the momentum transfer (green and blue) in comparison to full multiplet calculations (lines) for a $\Gamma_7^-$ ground state. c) and d) difference plots compared to $\Gamma_7^-$ (orange lines) and $\Gamma_7^+$ simulation (grey lines). Quantitative agreement for $CeCoIn_5$ is only achieved when mixing some of the excited $\Gamma_7^+$ into the dominantly $\Gamma_7^-$ ground state.*

experiments were performed at the Max-Planck beamline P01 at PETRA-III in Hamburg.

Figure 2 shows the directional dependence of the $N_{4,5}$ signal for the momentum transfers in 100 and 110 directions and the comparison with a full multiplet calculation. We find that the $\Gamma_7^-$ with its lobes along the (110) direction forms the ground state. Our finding suggests that the hybridization with the out-of-plane In2 atoms is most important, but that also hybridization with the in-plane In1 is non-negligible (see Fig. 1). The latter supports our findings of the $CeCo(In_{1-y}Sn_y)_5$ substitution series [1]. We further find that the directional dependence in $CeCoIn_5$ is not only smaller due to the different $J_z$ admixture of the ground state. It is also diminished by the *cf*-hybridization induced intermixing of the first excited state into the ground state [2], thus raising the question about the effective ground state degeneracy.

**Search for multiorbital ground state in $CeCu_2Si_2$ [6]**

Unconventional, heavy-fermion superconductivity in $CeCu_2Si_2$ was discovered in 1979 by Steglich *et al*. and has been intensively investigated since. The ambient or low-pressure superconducting phase is close to antiferromagnetism so that it is likely that spin fluctuations are responsible for the formation of Cooper pairs. There is strong evidence for the *d*-wave character of the ambient pressure superconducting phase. More recently, the *d*-wave nature of the ambient pressure superconducting phase in $CeCu_2Si_2$ has been contested, and here the detailed investigation of the crystal-field wave functions comes into play ([6] and references therein). A *multiorbital* ground state consisting of a $\Gamma_7$ with some contribution of the $\Gamma_6$ symmetries would allow *d+d* singlet pairing which could accommodate the experimental findings of all groups.

We have investigated the linear dichroism in XAS of a superconducting $CeCu_2Si_2$ sample at beamlines at SOLEIL in St Aubin, ALBA in Barcelona, and NSRRC in Taiwan, to cover a very wide temperature range from 250mK to 250K, i.e. from well below the superconducting transition at $T_c$=600mK to well above the Kondo temperature $T_K$=20K. The linear dichroism is well described by a $\Gamma_7$ ground state and the thermal occupation of excited states at about 30 meV. The crystal-field scheme does not change throughout the entire temperature range, thus, making any scenario of orbital switching (as proposed in the literature) highly unlikely. Spectroscopic evidence for the Ce $4f^0$ configuration in the ground state is consistent with the possibility for a multiorbital character of the ground state. We estimate from the Kondo temperature and crystal-field splitting energies that several percent of the higher lying $\Gamma_6$ and $\Gamma_7^2$ crystal-field states contribute to the primary $\Gamma_7^1$ ground state. This estimate is also supported by renormalized band-structure calculations that uses the experimentally determined crystal-field scheme.

**Low energy excitations in Kondo insulators – $SmB_6$ and $CeRu_4Sn_6$ [7, 8]**

Kondo insulators are a special class of *f*-electron compounds with strong *cf*-hybridization. In Kondo insulators the Fermi level lies in the hybridization gap so that the materials become insulating (or semi metallic) when the hybridization becomes effective at low *T*. Some Kondo insulators have experienced a great revival in recent years due to the exciting prediction that they have all the ingredients, namely strong spin-orbit coupling and crossing bands of opposite parity, the 4*f* and the 5*d*, for being strongly correlated topological insulators (scTI). We, therefore, investigated the low energy excitations of $SmB_6$, and of $CeRu_4Sn_6$ with high resolution resonant inelastic x-ray scattering (RIXS) at the state-of-the art beamline ID32 at ESRF, Grenoble, France [7, 8]. In both cases the efforts of neutron scattering were limited despite the much better resolution. Either strong absorption, strongly broadened excitations, or the superposition of two valence states in case of intermediate valent Sm in $SmB_6$ hampered the neutron results. RIXS, on the other hand, is element and configuration specific, and also

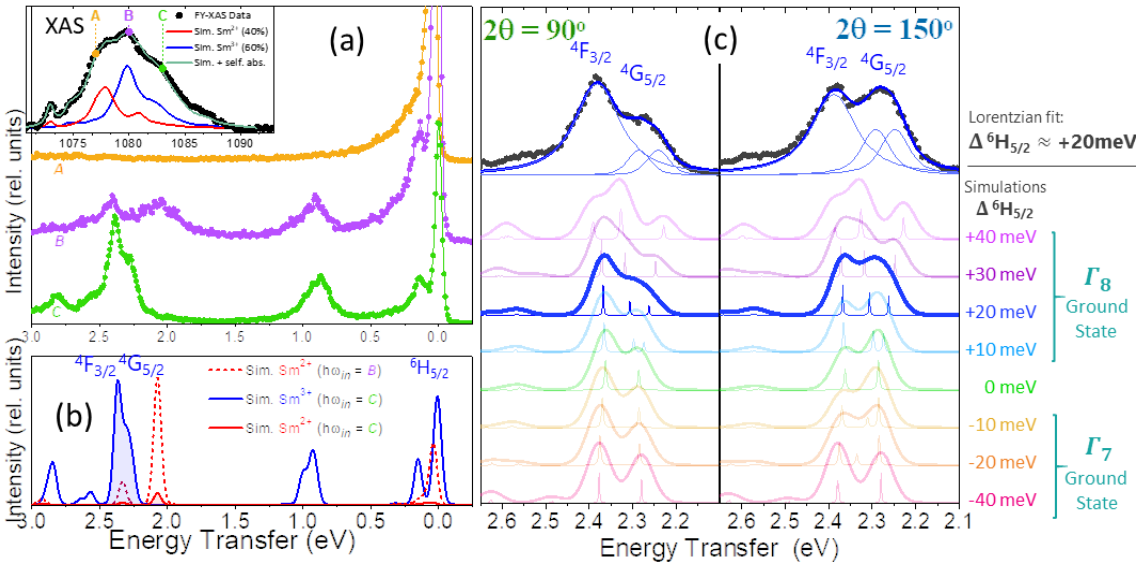


*Fig. 3: (a) RIXS spectra of $SmB_6$ for three incident energies (see orange, purple and green dots in inset). Inset: $M_5$ FY XAS spectrum, reproduced with 60% $Sm^{3+}$ (blue) and 40% $Sm^{2+}$ (red). (b) simulated $Sm^{3+}$ (solid blue line) and $Sm^{2+}$ (red) RIXS spectra for two incident energies. (c) Top: RIXS data (grey dots) of $^4F_{3/2}$ and $^4G_{5/2}$ multiplets overlaid with a fit of three Lorentzian lines. Bottom: full multiplet simulations for different crystal-field splittings. A corresponding splitting of +20meV of the $^6H_{5/2}$ multiplet gives the best agreement; the + sign refers to the quartet ground state.*

bulk sensitive. In the following we will focus on our RIXS study of the most promising scTI candidate $SmB_6$.

With RIXS the $Sm^{2+}$ intensity of Sm in $SmB_6$ can be suppressed and an almost pure $Sm^{3+}$ RIXS signal can be obtained by choosing an incident energy on the higher energy tail of the Sm $M_5$ edge (see Fig. 3(a) and (b)). We further took advantage of the large energy transfer range of RIXS and the large number of multiplets of Sm (see Fig. 3 (b). We analyzed the $^4G_{5/2}$ multiplet at about 2.3eV because it has the same total orbital momentum as the ground state multiplet $^5H_{5/2}$ so that the same crystal-field parameters determine the splitting, but it has a splitting that is enlarged by a factor of about 2.2 due to the larger Stevens-type factor. Comparing the data with full multiplet calculations that consider different crystal-field splittings (see Fig. 3(c)), and cross-checking this analysis with an empirical fit of three Lorentzian lines, one for the $^4F_{3/2}$ and two of identical width for the splitting of the $^4G_{5/2}$, we find a crystal-field splitting of (20±10) meV for the $Sm^{3+}$ $^5H_{5/2}$ Hund's rule ground state. We further confirm the $\Gamma_8$ quartet nature of the ground state that our group had previously found with the NIXS technique [9]. This RIXS result has interesting consequences. It suggests that the 4*f* band width is of the same energy scale, thus, the search for topological surface states should not focus only on bands with strong dispersion. Furthermore, these findings give guidance to theory, namely to not only reproduce the very narrow bands but to also produce the correct ground state symmetry.

**Hidden order and the systematics in the U$M_2Si_2$ family [10]**

The interplay of band-formation and electron-correlation effects in uranium heavy fermion compounds is an intellectual challenge. The question is, should the modelling start with band theory or a local atomic approach? This has been particularly troublesome because neither the presence nor the symmetry of the active atomic-like states was so far experimentally accessible nor are there generally accepted numbers for the filling of the 5*f* shell. In the present study unexpected insight has been gained from advanced spectroscopies (NIXS and HAXPES) on isostructural members of the U$M_2Si_2$ family with different properties. We studied the Pauli paramagnet $UFe_2Si_2$, the hidden order compound $URu_2Si_2$, and the large-moment antiferromagnets $UNi_2Si_2$ and $UPd_2Si_2$.

We had previously shown that beyond dipole NIXS at the U $O_{4,5}$ edge (5*d*→5*f*) reveals a singlet ground state of either the $\Gamma_2$ symmetry or the $\Gamma_1$ of majority $J_z = |+4\rangle \pm |-4\rangle$ in $URu_2Si_2$ [11]. Figure 4(a) shows the directional dependent NIXS spectra of the four U$M_2Si_2$ (*M*=Fe, Ni, Ru, Pd) compounds that were measured at

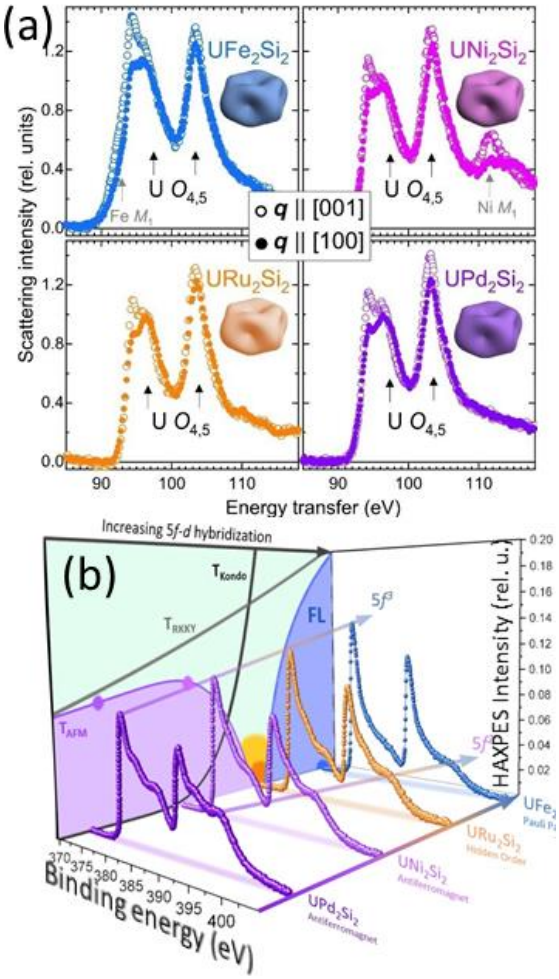


*Fig. 4: (a) NIXS spectra and respective electron densities of $UM_2Si_2$, M=Fe, Ni, Ru, and Pd. (b) HAXPES spectra (same colour code as (a)) with $f^2$ Doniach phase diagram in the background [10].*

the MPI beamline P01 at DESY/PETRA-III in Hamburg. We find that all four compounds share the same ground state symmetry of the crystal-field split U $f^2$ configuration (note that the difference in the $UFe_2Si_2$ data at about 95eV is due scattering of the Fe $M_1$ transition). Hence, the different properties of the $UM_2Si_2$ are not due to different ground state symmetries. We show that a quasi-doublet consisting of the two singlet states, $\Gamma_2$ and $\Gamma_1$ of majority $J_z = |+4\rangle \pm |-4\rangle$, can induce large-moment magnetism as in $UNi_2Si_2$ and $UPd_2Si_2$, as well as the hidden order in $URu_2Si_2$. HAXPES, on the other hand (see Fig. 4(b)), shows a systematic increase of U $5f^3$ weight from Pd→Ni→Ru→Fe, indicating increasing itineracy. Combining the results of NIXS and HAXPES led us to propose a systematics (see phase diagram in Fig 4(b)) which provides some understanding why e.g. Ru with pressure becomes antiferromagnetic and why a large moment emerges [10].

Hence, local-moment systems (*M*=Ni, Pd) highlight the local atomic aspects of the electronic structure while Pauli paramagnets (*M*=Fe) reflect the importance of band formation but with bands that are strongly renormalized due to the remnant local aspect. $URu_2Si_2$, with its hidden order and superconductivity, is in-between these two regimes. The above findings demonstrate the validity of the concept *the dual nature of U 5f electrons* for this set of U compounds.

**External Cooperation Partners**

MPI agreement with DESY, PETRA-III, Hamburg for beamline P01. Consortium agreement with P. Ohresser for mK insert at beamline DEIMOS at synchrotron SOLEIL, Saint Aubin, France.

**References**


[1] *Evolution of ground-state wave function in $CeCoIn_5$ upon Cd or Sn doping, K. Chen, F. Strigari, M. Sundermann, Z. Hu, Z. Fisk, E. D. Bauer, P. F. S. Rosa, J. L. Sarrao, J. D. Thompson, J. Herrero-Martin, et al., Phys. Rev. B **97** (2018) 045134.*

[2]* *Orientation of the ground state orbital in $CeCoIn_5$ and $CeRhIn_5$, M. Sundermann, A. Amorese, F. Strigari, B. Leedahl, L. H. Tjeng, M. W. Haverkort, H. Gretarsson, H. Yavas, M. Moretti Sala, E. D. Bauer, et al., Phys. Rev. B **99** (2019) 235143 - Editors' Suggestion.*

[3] *Correlation between ground state and orbital anisotropy in heavy fermion materials, T. Willers, F. Strigari, Z. Hu, V. Sessi, N.B. Brookres, E.D. Bauer, J.L. Sarrao, J. D. Thompson, A. Tanaka, S. Wirth, et al., Proc. Natl. Acad. Sci. U.S.A. **112** (2015) 2384.*

[4] *The quartet ground state in $CeB_6$: an inelastic x-ray scattering study, M. Sundermann, K. Chen, H. Yavas, H.-O. Lee, Z. Fisk, M. W. Haverkort, L. H. Tjeng, and A.Severing, Euro Phys. Lett. **117** (2017) 17003.*

[5] *Determining the In-Plane Orientation of the Ground-State Orbital of $CeCu_2Si_2$, T. Willers, F. Strigari, N. Hiraoka, Y. Q. Cai, M.W. Haverkort, K.-D. Tsuei, Y. F. Liao, S. Seiro, C. Geibel, F. Steglich, et al., Phys. Rev. Lett **109** (2012) 046401.*

[6]* *Possible multiorbital ground state in $CeCu_2Si_2$, A. Amorese, A. Marino, M. Sundermann, K. Chen, Z. Hu, T. Willers, F. Choukani, P. Ohresser, J. Herrero-Martin, S. Agrestini, et al., Phys. Rev. B **102** (2020) 245146 – Editors' Suggestion.*

[7]* *Determining the local low-energy excitations in the Kondo semimetal $CeRu_4Sn_6$ using resonant inelastic x-ray scattering, A. Amorese, K. Kummer, N.B. Brookes, O. Stockert, D. T. Adroja, A.M. Strydom, A. Sidorenko, H. Winkler, D. A. Zocco, A. Prokofiev, et al., Phys. Rev. B **98** (2018) 08116(R).*

[8]* *Resonant inelastic x-ray scattering investigation of the crystal-field splitting of $Sm^{3+}$ in $SmB_6$, A. Amorese, O. Stockert, K. Kummer, N. B Brookes, D.-J. Kim, Z. Fisk, M. W. Haverkort, P. Thalmeier, L.H. Tjeng, and A. Severing, Phys. Rev. B **100** (2019) 24107(R).*

[9] *4f Crystal Field Ground State of the Strongly Correlated Topological Insulator $SmB_6$, M. Sundermann, H. Yavaş, K. Chen, D. J. Kim, Z. Fisk, D. Kasinathan, M. W. Haverkort, P. Thalmeier, A. Severing, and L. H. Tjeng, Phys. Rev. Lett.* ***120*** *(2018) 016402.*

[10]* *From antiferromagnetic and hidden order to Pauli paramagnetism in $UM_2Si_2$ compounds with 5f electron duality, A. Amorese, M. Sundermann, B. Leedahl, A. Marino, D. Takegami, H. Gretarsson, A. Gloskovskii, C. Schlueter, M. W. Haverkort, Y. Huang, et al., Proc. Natl. Acad. Sci. U.S.A.* ***117*** *(2020) 30220.*

[11] *Direct bulk-sensitive probe of 5f symmetry in $URu_2Si_2$. Proc., M. Sundermann, M. W. Haverkort, S. Agrestini, A. Al-Zein, M Moretti Sala, Y. Huang, M. Golden, A. deVisser, P. Thalmeier, L.H. Tjeng, and A. Severing, Proc. Natl. Acad. Sci. U.S.A.* ***113*** *(2016) 13989.*

[#] severing@cpfs.mpg.de

[##] hao.tjeng@cpfs.mpg.de