Supplemental Material to

Experimental observation of 5*f* valence fluctuations by high-resolution XAS in UPd_2Cd_{20}

Y. Hirose,[1,2] F. Honda,[3] H. Doto,[4] N. Kawamura,[5] K.O. Kvashnina,[6,7] L. Amidani,[6,7] K. Uhlířová,[8] J. Kolorenč,[9] L. Havela[8,*]

[1] Department of Physics, Niigata University, Niigata 950-2181, Japan
[2] Materials Sciences Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki, 319-1195
[3] Central Institute of Radioisotope Science and Safety, Kyushu University, Fukuoka 819-0395, Japan.
[4] Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan
[5] Japan Synchrotron Radiation Research Institute, Hyogo, Sayo 679-5198, Japan
[6] Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Dresden 01313, Germany
[7] The Rossendorf Beamline at the European Synchrotron (ESRF), F-38043 Grenoble, France
[8] Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, 121 16 Prague 2, Czech Republic
[9] Institute of Physics, Czech Academy of Science, Na Slovance 2, 182 00 Prague 8, Czech Republic

* Contact author: ladislav.havela@matfyz.cuni.cz

Ab-initio calculations of UPd_2Cd_{20} – density functional theory

We consider here the issue why the valence fluctuating state is not more common among uranium compounds. In rare earths, it appears when the hybridization of the *f*-states with the conduction electron states is weak but not entirely negligible. Somewhat stronger hybridization would lead to a conventional band state with a non-integer *f*-states occupancy. Such a regime, which is generic in systems based on Ce, Yb or on other so-called anomalous rare earths, is rather unusual in light actinides, where the tendency to 5*f* delocalization is much stronger.

The valence fluctuating state is inherently a multi-reference state and as such it cannot be predicted or characterized by conventional density-functional theory (DFT) calculations. It is nevertheless possible to use DFT to estimate the general bonding situation, which sets the stage on which the exotic phenomena can develop. To this end, we performed DFT calculations at the experimental volume, using Wien2k package [1] that implements the linearized augmented plane-wave method and its extensions, and combines a scalar-relativistic description with the spin-orbit coupling. We used the spin-polarized local density approximation (LSDA) for the exchange-correlation functional. The parameters determining the accuracy of the DFT calculations were: the radii of the atomic (muffin-tin) spheres were $R_{MT}(U) = 3.0\ a_B$ and $R_{MT}(Pd) = R_{MT}(Cd) = 2.6\ a_B$, the basis-set cutoff K_{max} was defined with $R_{MT} \times K_{max} = 8.0$, and the Brillouin zone was sampled on a *k*-point mesh 11 × 11 × 11. The default Wien2k basis set with local orbitals for semi-core states U 6*s*, 6*p*, Pd 4*p* and Cd 4*p* was used.

The results, seen in Fig. S1, reveal a magnetic ground state (a colinear ferromagnetic ordering was considered for simplicity – the local electronic structure at the uranium atom probed by the absorption spectroscopies we discuss will be quite similar in the ferromagnetic and antiferromagnetic states). The U-5*f* states, concentrated into a rather narrow band near the Fermi level, have a filling $n_{5f} = 2.7$. The exchange splitting yields the spin moment of 1.1 per U atom and the antiparallel orbital moment of 3.9 per U atom when the moments are determined from the integrals of the electron density over the uranium atomic sphere. Both spin-up and spin-down 5*f* sub-bands are only about 1 eV wide and weakly hybridized with the Pd-4*d* states, concentrated around 3 eV below the Fermi level, as well as with the Cd-4*d* states, located as deep as 8 to 10 eV below E_F. In general, this is the situation in which incipient 5*f* localization can be expected.

The 5*f* band width of 1 eV deduced from LSDA (Fig. S1) is contributed to by the hybridization as well as by the Zeeman-like splitting of the 5*f* shell caused by the exchange field. To isolate only the

hybridization-induced band width, we performed spin-restricted (non-magnetic) LDA calculation. The corresponding 5*f* DOS (shown also in Fig. S1) consists of well separated $5f_{5/2}$ and $5f_{7/2}$ peaks in this case, both having their band width smaller than 0.5 eV, resembling the 4*f* bands in rare-earth compounds.

Finally, we show the unoccupied part of the U $6d_{5/2}$ density of states from the LSDA calculation, which represents an approximation to the L_3-edge absorption spectrum (Fig. S2). The line shape obtained by the appropriate broadening of this DOS due to a finite instrument resolution (Gaussian with 0.9 eV of full width at half maximum) and due to a finite lifetime of the $3d_{5/2}$ core hole remaining in the final state of the HERFD measurement (Lorentzian with 3.3 eV of full width at half maximum [2]) is indeed close to the shape of the two components obtained by fitting the experimental spectra (Fig. 2).

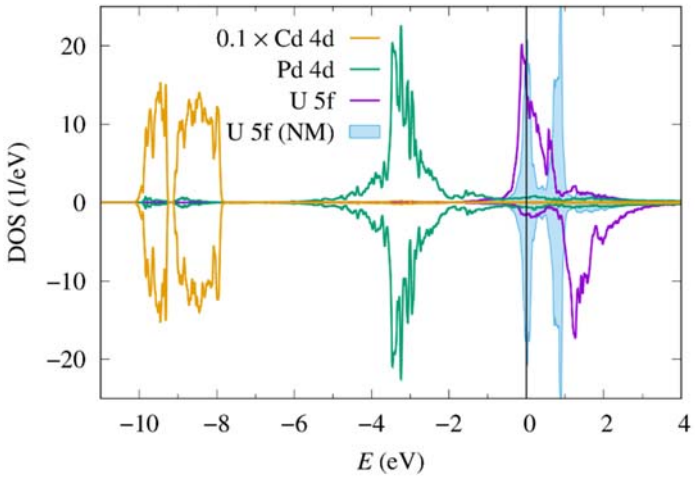

FIG S1. Orbital-resolved density of states of UPd_2Cd_{20} obtained by LSDA calculation (thick lines) and by LDA calculation (filled curve). The Cd 4*d* DOS is reduced ten times to allow plotting at the same scale. Positive DOS values correspond to the majority-spin states, negative values to the minority-spin states.

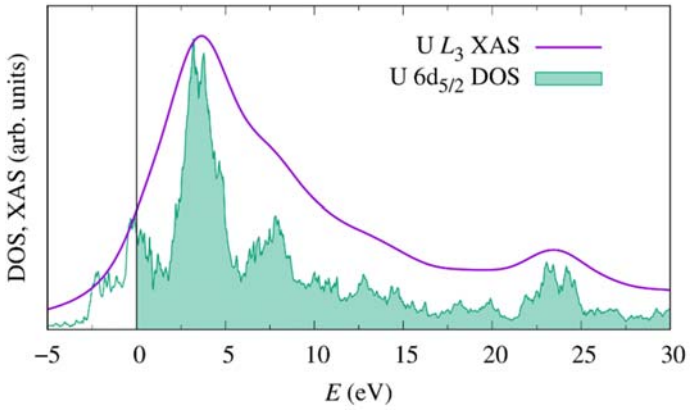

FIG S2. Uranium $6d_{5/2}$ density of states from the LSDA calculation (green) and the appropriately broadened unoccupied part of this DOS (violet) approximating the U L_3 absorption spectrum.

[1] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G. K. H. Madsen, and L. D. Marks, WIEN2k: An APW+lo program for calculating the properties of solids, J. Chem. Phys. **152**, 074101 (2020).

[2] P.-A. Raboud, J.-Cl. Dousse, J. Hoszowska, and I. Savoy, Phys. Rev. A **61**, 012507 (1999).