Supporting information

Sensitivity to actinide doping of uranium compounds by resonant inelastic x-ray scattering at U L_3 edge

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This document provides information about additional first-principles calculations performed with the aim to verify the precision of the results, presented in the main text of the article.

The LMTO-ASA method, employed in the current study, contains geometrical constraints on the shape of the potential inside the muffin-tins spheres. The method is very robust and has relatively small computational load. It is often argued, however, that this method is less accurate than the full-potential (FP) ones, which treat the potential exactly. In order to assess the degree of precision of the obtained results, we have performed a set of calculations using the FP realisation of the LMTO method (details of the implementation can be found in Ref. 1). In addition to that, the impact of the spin-orbit coupling (SOC) on the valence band DOS's was investigated.

Uranium dioxide was taken as a reference system. The unit cell geometry, exchange-correlation functional and the on-site Coulomb interaction parameters were chosen to be the same in both codes. In the FP-LMTO calculations, each electronic state was described with

the set of two or three basis functions, thus the overall size of the basis was more than two times larger than in the LMTO-ASA calculations.

In Table S1 we show the comparison between the calculated values of the magnetic moments.

Method	Setup	Magnetic moment (μ_B)
LMTO-ASA	**LDA+U**	**1.91**
FP-LMTO	**LDA+U**	**1.86**
FP-LMTO	**LDA+U+SOC**	**1.95**

Table S1. Calculated magnetic moment per U atom in AFM UO_2, obtained for various computational setups. For the calculations with SOC the values of the total moment *J* are shown.

One can see that the values of the total moment delivered by different codes and methods are very close to each other. The differences can partially be attributed to the different choice of the MT spheres, where the projections are performed. When SOC is included, the value of the magnetic moment remains the same, but its nature is drastically different. In this case the orbital moment (2.83 μ_B) gives the main contribution to the total moment, being antiparallel to the spin one (-0.83 μ_B).

Calculated DOS of the selected orbitals are shown in Fig. S1. The overall shape of the DOS curves agree with each other fairly well. Most of the differences emerge in the unoccupied sector 6 eV above the Fermi level. In this region there is a collective compression of the spectral features within FP-LMTO method as compared with the LMTO-ASA. However, these details are relatively small comparing to the instrumental resolution of our experiment. Since the data shown in Fig. S1 is going to be substantially broadened to mimic the

experimental situation, the simulated RIXS planes obtained with two DFT codes will barely be distinguishable.

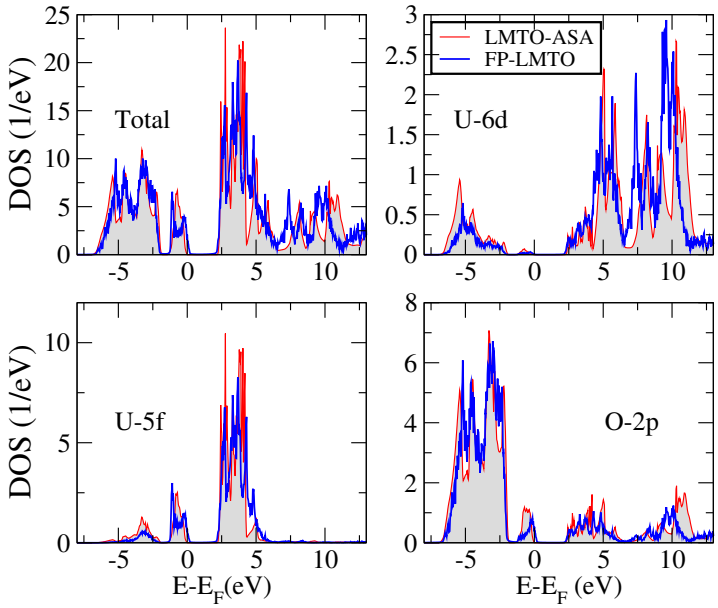

Figure S1. Comparison between the calculated DOS curves obtained by FP-LMTO and LMTO-ASA methods. LDA+U calculations have been performed in both cases. Fermi level (E_F) is set to zero. FP-LMTO results are in excellent agreement with the prior DFT calculations (Ref. 2).

The influence of spin-orbit coupling on the shape of the DOS was also studied. The comparison between LDA+U and LDA+U+SOC results is shown in Fig. S2. The results suggest that the spin-orbit coupling mainly influences well-localised *5f* orbitals. The modifications of the itinerant *6d* states are marginal and are well below the experimental resolution.

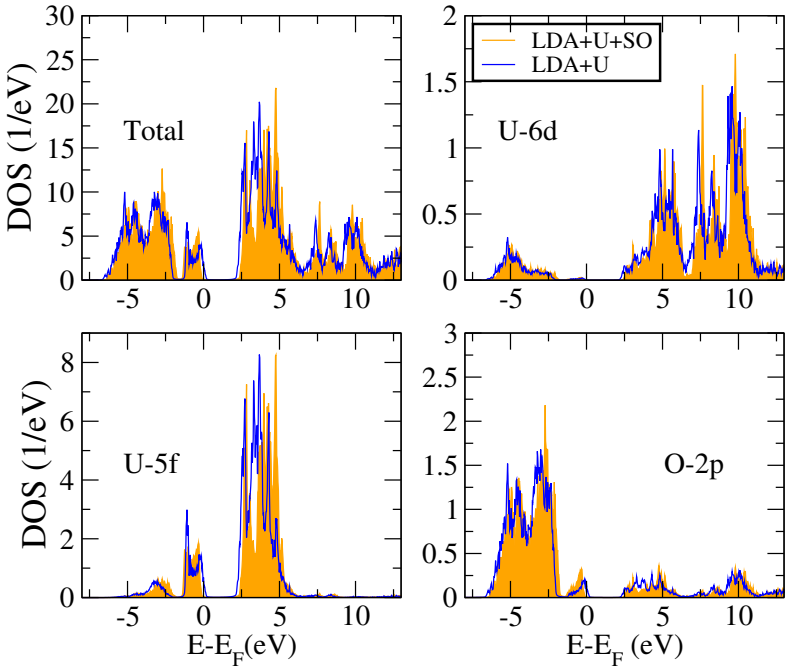

Figure S2. Calculated DOS for selected orbitals obtained within the LDA+U and LDA+U +SOC methods.

REFERENCES

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