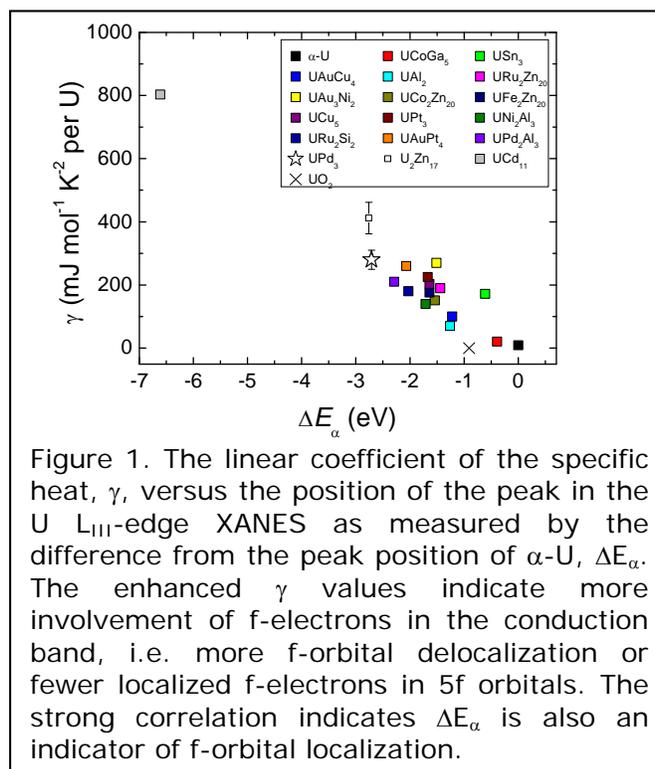


Illuminating the Multiconfigurational Ground State of Element and Intermetallic Compounds of U and Pu

The structural, electronic, and magnetic properties of U and Pu elements and intermetallics remain poorly understood despite decades of effort, and currently represent an important frontier of condensed matter physics. The last decade has seen great progress both due to the discovery of superconductivity in PuCoGa₅ at 18 K¹ and advances in theory that finally can explain fundamental ground state properties in elemental plutonium, such as the phonon dispersion curve, the non-magnetic ground state, and the volume difference between the α - and δ -phases.² A new feature of the recent calculations is the presence not only of intermediate valence of the Pu 5f electrons, but of multiconfigurational ground states, where the different properties of the α - and δ -phases are primarily governed by the different relative weights of the 5f⁴, 5f⁵, and 5f⁶ electronic configurations. Utilizing the new 7-crystal Johann-type spectrometer on BL 6-2 at SSRL, resonant x-ray emission spectroscopy (RXES) data have been collected by Corwin Booth (Lawrence Berkeley National Laboratory) and a team of researchers from Lawrence Berkeley, Los Alamos and Lawrence Livermore National Laboratories, and SSRL that show, for the first time, spectroscopic signatures of each of these configurations and their relative changes in PuSb₂, α - and δ -Pu. In combination with similar data on UCd₁₁ and UCoGa₅, as well as conventional x-ray absorption near-edge structure (XANES) spectra on a wide variety of uranium and plutonium intermetallic compounds, these data indicate such states may be ubiquitous in uranium and plutonium intermetallics, providing a new framework toward understanding properties ranging from heavy fermion behavior, superconductivity, and intermediate valence to mechanical and fundamental bonding behavior in these materials.

The usual method for measuring multiconfigurational states in the lanthanides (Ln's) is to measure the Ln L_{III}-edge XANES. When configurations differing by one electron exist, their energies are split by the core hole in the final state. The two resulting resonances are easily identified in XANES spectra because their energy separation is about 10 eV, while the broadening of the final state is only about 4 eV. The situation is reversed, however, for the actinides (An's), where the splitting is expected to be about 4 eV, but the broadening is about 8 eV. Nevertheless, clear edge shifts are observed between many intermetallic U (Figure 1) and Pu compounds.

Advances in RXES have now allowed for spectra with sufficient resolution to resolve individual resonances associated with the various An valence states. In this experiment, the fluorescing L _{α 1} x-rays are resolved to better than 2 eV, allowing the individual configuration resonances to be separated as both a function of incident (E_i) and



emission (E_E) photon energy. By taking advantage of the resonant characteristics of these features, the contribution of three configurations are clearly observed. By integrating the individual configuration contributions over both E_I and E_E , the normalized contribution from each configuration can now be obtained. For example, the contribution from each configuration in δ -Pu is, in fact, substantial: the $5f^4$, $5f^5$, and $5f^6$ contributions are 19%, 46%, and 35%. The weighted average (f-occupancy $n_f=5.28$) is in reasonable agreement with DMFT calculation² ($n_f=5.2$).

This work opens the door to considering multiconfigurational ground states to explain other mysterious behavior in U and Pu materials, such as the hidden-order state in URu_2Si_2 , or the nature of superconductivity in $PuCoGa_5$. Also, as a fundamental property of U and Pu, these results are perhaps most important for understanding the nature of the relative importance of the delocalizing effect of relativity and the localizing effect of symmetry in 5f orbitals.

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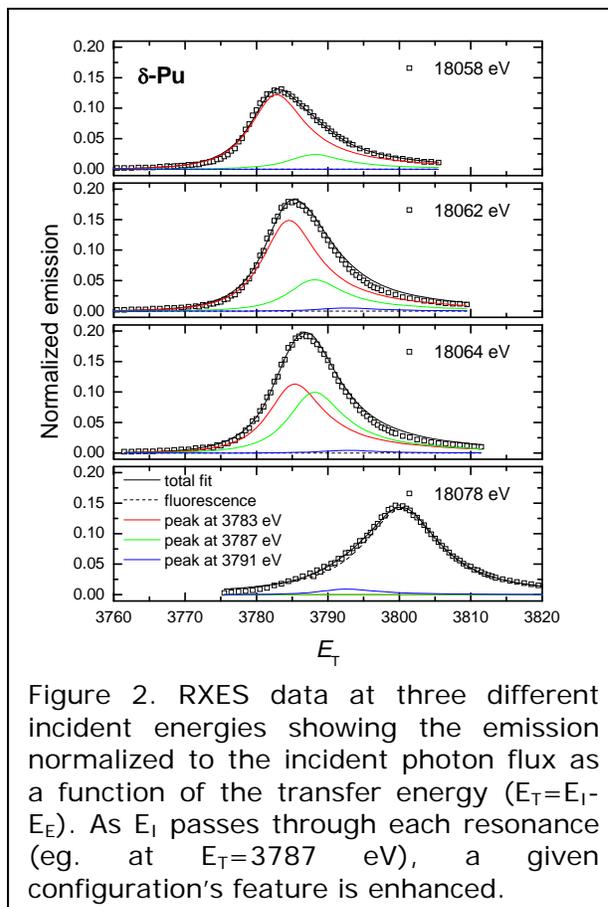


Figure 2. RXES data at three different incident energies showing the emission normalized to the incident photon flux as a function of the transfer energy ($E_T=E_I-E_E$). As E_I passes through each resonance (eg. at $E_T=3787$ eV), a given configuration's feature is enhanced.

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