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Anomalous dispersion and band gap reduction in UO_{2+x} and its possible coupling to the coherent polaronic quantum state

Steven D. Conradson [a,*], David A. Andersson [b], Paul S. Bagus [c], Kevin S. Boland [b], Joseph A. Bradley [b], Darrin D. Byler [b], David L. Clark [b], Dylan R. Conradson [b], Francisco J. Espinosa-Faller [d], Juan S. Lezama Pacheco [b], Mary B. Martucci [b], Dennis Nordlund [f], Gerald T. Seidler [e], James A. Valdez [b]

[a] Synchrotron Soleil, Saint-Aubin BP-48, 91192, France
[b] Los Alamos National Laboratory, Los Alamos, NM 87545, United States
[c] University of North Texas, Denton, TX 76203, United States
[d] Universidad Marista de Merida, Merida, Yucatan 97300, Mexico
[e] University of Washington, Seattle, WA 98195, United States
[f] SLAC National Accelerator Laboratory, Menlo Park, CA 94025, United States

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ABSTRACT

Hypervalent UO_2, $UO_{2(+x)}$ formed by both addition of excess O and photoexcitation, exhibits a number of unusual or often unique properties that point to it hosting a polaronic Bose–Einstein(-Mott) condensate. A more thorough analysis of the O X-ray absorption spectra of UO_2, U_4O_9, and U_3O_7 shows that the anomalous increase in the width of the spectral features assigned to predominantly U 5*f* and 6*d* final states that points to increased dispersion of these bands occurs on the low energy side corresponding to the upper edge of the gap bordered by the conduction or upper Hubbard band. The closing of the gap by 1.5 eV is more than twice as much as predicted by calculations, consistent with the dynamical polaron found by structural measurements. In addition to fostering the excitation that is the proposed mechanism for the coherence, the likely mirroring of this effect on the occupied, valence side of the gap below the Fermi level points to increased complexity of the electronic structure that could be associated with the Fermi topology of BEC–BCS crossover and two band superconductivity.

1. Introduction

As the origin of many of the interesting properties of matter, covalency is as important as it is awkward to define [1]. In classic real space physics, if the role of quantum mechanics is to define the distribution of electrons but the forces are electrostatic, then covalency is the accumulation of electron density between the nuclei that renders the overall force between the atom pair attractive. An important factor is therefore the spatial extent of the original atomic orbitals since their overlap determines the shared volume available for building up the charge. The concept of covalency is more easily depicted in momentum space as the shifts in the energy levels of the molecular orbitals from their parent atomic states in molecules and the dispersion of the bands in condensed systems. The structures of transition metals possessing localized electrons in flat bands tend to be defined by the longer range magnetic interactions of the isolated spins. In contrast, delocalized, itinerant electrons can interact directly to give bands with large dispersions, with bulk properties that result from these bonds. Elements in the crossover region are the ones that display polymorphism, complicated magnetism, chemically reactive electronic states, and other manifestations of correlated electrons.

The rare earth elements, whose frontier 4*f* orbitals are confined to the core of the atom, and the heavier actinides whose 5*f* orbitals are similarly constrained therefore for the most part behave in predictable and relatively unexciting ways. The lighter actinides are, however, the opposite, with one example being the radical change in atomic radius at plutonium [2,3]. Residing at the crossover between spatially extended and localized 5*f* orbitals, it is the most complex element in the periodic table with six solid phases encompassing monoclinic to fcc symmetries, two of which exhibit negative thermal expansion coefficients, that span a 22% range of densities before it melts from the bcc ε phase into a higher density liquid at a relatively modest 912.5 K. In addition to this evidence for the ambiguity in the ability of the 5*f* states to overlap, it has also recently been shown that the absence of the predicted magnetism

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[*] Corresponding author.

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in Pu is because the temporal fluctuations that create hybridized or mixed electronic states in dynamical mean field theory appear to have physical significance, scrambling the spins faster than they can collectively orient [4]. It would not be surprising if these two phenomena, one in time and one in space, are coupled. This pattern of diversity is also displayed in their chemistry. Pm-Am exhibit an usually large number of valences in their chemical compounds that are correlated with a radical change in bonding and symmetry from spherical and highly ionic in their (III) and (IV) states to the highly oblate (trans di-) oxo moiety with the ultra short, triply bonded oxo ion for (V)–(VII), or a tetraoxo configuration under certain conditions [1,5].

Analogous to Pu metal, the most complicated binary metal oxide phase diagram may be that for U [6,7] where there is not even consensus whether the number of distinct compounds between $UO_{1.5}$ and UO_3 is greater than 20 [8] or not [9]. It divides into two regions. Below $UO_{2.33-2.5}$ the structures are strictly or approximately cubic. At temperatures below those where rapid O diffusion eliminates crystallographic disorder there are two mixed valence compounds that are single phase in diffraction, U_4O_9 and U_3O_7, although the multiplicity of their extended superlattices has prevented their structures from being completely solved [10–14]. Even in this ionic region, however, there are indications of more complexity, such as superionic conductivity of UO_{2+x} and the aggregation of the adventitious O in UO_{2+x} so that it is better described as UO_2:U_4O_9 and U_4O_9:U_3O_7 mixtures [10,15,16]. At higher O:U ratios the structures are layered because of the propensity of U(V) and (VI) to form the trans dioxo species. Another unusual or even unique anomaly is the loss of the normal correlation between valence and geometry/bond length in the higher oxides. In molecular or coordination compounds the U—O bonding patterns are quite rigid with the distances falling into ranges of only a few hundredths of an Å, [5] with the only suggestion of flexibility being a small expansion of the U-oxo bond that is coupled to greatly increased lability in hydroxide complexes [17]. However, in the solid state the α phase of UO_3 is highly oblate with an extremely short reported 1.64 Å U-oxo distance, [18] whereas the δ phase prepared by a slightly different procedure places the U ions in fully octahedral sites with U—O equals 2.08 Å, [19] with the intermediate phases giving intermediate distances in less distorted sites [20,21]. If the ternary uranates are included, [22–25] U(VI) exhibits essentially a continuous range of U—O bond lengths from 1.64 to 2.45 Å and longer. U(V) displays a continuous range of U—O distances from 1.9 to 2.7 Å in a single compound, U_2O_5. This behavior implies an exceptionally flat U—O potential for the higher valences that is highly susceptible to small changes in other factors influencing the structure and that can shift quite easily in response to such factors. It also implies a large degree of what would most likely be termed covalency; hard spherical ions do not change their conformations because of interactions with their neighbors. The shortness of the U-oxo bond points to a predilection for covalency that could potentially be distributed to other bonds if it is diminished in that one.

These properties of U(V) and (VI) that stabilize them in layered structures and the way they combine with the much less covalent U(IV) ions [26] with their cubic or spherical geometries underlie the special flexibility of the (1 1 1) planes in UO_2 [27]. Not only do dislocation loops form along them, [28] but their easy [1 1 1] expansion also causes substitutional cations that prefer octahedral environments, e.g., Cr^{3+}, to cluster along them as well. This behavior establishes the environment that promotes the dynamical polaron in fluorite structured, chemically or photodoped $UO_{2(+x)}$ [29,30]. The 2 U(V) ↔ U(IV) + U(VI) disproportionation excitation of these polarons would occur easily via the transfer of O ions between their buckled-apical positions for fluorite and planar-apical positions for layered, triggered by a [1 1 1] type acoustic phonon that causes the separation of the (1 1 1) U planes to oscillate. The synchronization of this internal reaction throughout the U_4O_9-type domain formed by the aggregation of the adventitious O or photoinduced charges then gives the coherence that defines the polaronic Bose–Einstein(-Mott) condensate. We have previously reported the O XAS of UO_{2+x} that demonstrated a significant enhancement of the widths of the U 5*f* states in the upper Hubbard band (UHB, the conduction band) that is opposed to the trend of narrower spectral features with increasing charge [29] that we attributed to the mixing of the electronic states and increased dispersion that occurs with a dynamical polaron [31]. We now examine these results in greater detail to show that this increased dispersion specifically reduces the lower boundary of the UHB. This substantial reduction of the gap energy and the increased DOS within the UO_2 gap would then facilitate the excitation that results in the condensate formation [30]. In addition, it is likely that the cause of this effect acts on additional U 5*f* states so that it is mirrored in the lower Hubbard band (LHB, valence band). This would be of significant interest because much recent work on BEC–Barden–Cooper–Schrieffer (BCS) superconducting condensate crossover in mixed valence metal oxide and chalcogenide exotic superconductors is focused on the character of these bands closest to the Fermi level [32] and its implications for two band superconductivity [33–39].

2. Experimental and calculation methods

Samples were prepared and NIXS and XAS experiments were performed as previously described, [29,40–42] as were the calculations [43].

3. Results and discussion

3.1. O XAS of standards and UO_2

The O XAS of U-oxides [44–49] and even the oxo group of uranyl-containing molecules that are coordination complexes of U(VI) [50] consist of two principal features (Fig. 1). There is consensus not only for UO_2 but for all of them that, in agreement with theory, the lower energy feature around 530–535 eV originates in transitions to unoccupied states of the upper Hubbard band (UHB) that are predominantly U 5*f* in character and the higher energy feature around 537–543 eV in transitions to unoccupied states that are predominantly U 6*f*. This is true not only for UO_2 where the U is in a cubic site and the O surrounded by a tetrahedron of U, but also for layered compounds such as U_3O_8 with relatively long U—O_{oxo} bonds and α UO_3 with its extremely short one and even the oxo O ion in $Cs_2UO_2Cl_4$. The pattern is the result of the symmetry relationship between cubic and octahedral geometries where the latter results from locating a neighbor atom in the center of each of the six square that constitute the cube's sides whose corners are the eight vertices. It is also because the shift in energy between the different types of O, terminal oxo, symmetrically bridging oxo, asymmetrically bridging oxo, and planar O with varying coordination numbers and bond lengths is less than 1 eV. The increase in the width of the peaks in the layered oxides with their multiple O species relative to that of the single type of O in the uranyl tetrachloride is therefore not excessive. The spectral pattern is therefore preserved across all of these species because the differences in energies for the different O and U species are much smaller than their U 5*f*-5*d* separations that are relatively insensitive to the speciation and geometry [48].

The exception to this assignment is the small shoulder on the leading edge of the first peak. This was not assigned for $Cs_2UO_2Cl_4$ despite a very thorough set of experiments that utilized