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X-RAY ABSORPTION ON URANIUM SYSTEMS AT VARIOUS THRESHOLDS

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ABSTRACT. - We have studied the near edge X-ray absorption fine structure of various metallic and non-metallic U compounds at the L_3 , M_3 , $M_{4,5}$, $N_{4,5}$, and $O_{4,5}$ thresholds using transmission and total-electron-yield techniques. At the L_3 thresholds, a chemical shift of ≈ 4 eV between trivalent and tetravalent U compounds is observed, which drops to ≈ 2 eV between the latter and hexavalent U systems. This indicates extended 5f character and a 5f count close to two in the high oxidation states. The $M_{4,5}$ thresholds are characterised by intense absorption peaks due to 3d-5f transitions which show no multiplet structure from 3d-5f exchange interaction. However, the linewidths of the $M_{4,5}$ peaks decrease by $\approx 20\%$ with increasing U-U distance in metallic systems, indicating a narrowing of the 5f band. The soft X-ray absorption spectra at the $N_{4,5}$ thresholds behave very similarly to the $M_{4,5}$ edges, except for a vanishing intensity of transitions into the continuum. Rich structures from 5d-5f exchange interaction are observed at the $O_{4,5}$ edges of non-metallic U compounds, becoming broadened and partly vanishing in metallic systems, presumably due to the more itinerant nature of the 5f states.

I. INTRODUCTION

With the increasing availability of synchrotron radiation, X-ray absorption (XA) spectroscopy has become a valuable tool for studying the electronic structure of f and d electron systems. In particular, from the double-peaked structure of the L_3 edges in intermediate valent rare-earth (RE) compounds /1/, as well as characteristic multiplet patterns at the $M_{4,5}$ and $N_{4,5}$ edges /2/, detailed information on the 4f configuration has been obtained. For the actinides (An), the amount of available XA data is still limited, although dramatic changes in the M_5 edge shape at the α -to- δ phase transition in Pu metal have already indicated the sensitivity of XA to changes in the 5f electronic structure /3/. Since (in the keV range) XA can be performed on encapsulated samples, the method might gain importance under the aspect of providing an experimentally simple access to the electronic structure of the highly radioactive transuranium elements. Very generally, a transition from itinerant to localised character of the 5f states is anticipated at increasing An atomic number /4/, the details of which sensitively depend on the specific chemical environment and vary drastically among different compounds of the same An element. Photoemission (PE) and Bremsstrahlung Isochromat Spectroscopy (BIS), showed α -U as well as α -Pu metal to be itinerant 5f systems, while UO_2 displays localised 5f character /5/.

To further characterise the method in the An region and provide a basis for future investigations on transuranium systems, we have studied a variety of metallic and non-metallic U compounds by XA at the L_3 , M_3 , $M_{4,5}$, $N_{4,5}$ and $O_{4,5}$ thresholds. A value for the $2p/5f$ coulomb attraction is derived and details of the edge shapes are found to reflect changes in the nature of the $5f$ states across the various compounds. We conclude, that considerable information on the electronic structure of An systems may be obtained by XA.

II. EXPERIMENTAL

The L_3 and M_3 measurements were performed in transmission geometry at the ROEMO and EXAFS-2 beamline, respectively, of DESY/Hamburg. By mounting three ionisation chambers in series, the sample and a reference probe could be measured simultaneously for a highly accurate determination of relative energy shifts. The $M_{4,5}$, $N_{4,5}$ and $O_{4,5}$ edges were obtained by recording the total electron yield from the sample and -for normalisation purpose- from a 85% transmitting Au or Ni grid at the monochromator exit. The former measurements were performed at the JUMBO beamline of SSRL/Stanford, while the $N_{4,5}$ and $O_{4,5}$ edges were recorded at the SX-700 beamline of BESSY/Berlin. The energy resolution of the various monochromators at the respective thresholds is indicated by ΔE in Fig. 1; more details will be given in a forthcoming publication.

III. RESULTS AND DISCUSSION

For UF_4 an overview about the various thresholds investigated in this study is given in Fig. 1 on a relative energy scale. According to the dipole selection rules of XA and relative

Fig 1: XA spectra of UF_4 at various thresholds

density of unoccupied states (DOS), the transition at p and d thresholds, respectively, mainly map the $6d$ and $5f$ states in the presence of the core-hole. As suggested from this figure and found from comparing the L_3 and M_3 edges of various U compounds, both types of thresholds give consistent information on the (final state) $6d$ DOS. This is well expected from the local character of the core hole in both cases and the extended nature of the final states. Also seen in Fig. 1 are the M_5 and N_5 thresholds, reflecting the unoccupied $5f$ states. The great difference in the ratio of the "white line" (WL) to "edge jump" amplitudes between M_3 and M_5 demonstrates the much more localised character of the $5f$ states relative to $6d$. At the N_5 threshold, the intensity of transitions into the continuum is

vanishingly small, due to the larger wavefunction overlap of 5f states with 4d as compared to 3d states. Apparently, no multiplet splitting from core-hole/5f exchange interaction is resolvable at both, the M_5 and N_5 thresholds, in contrast to the RE $M_{4,5}$ edges. At the $O_{4,5}$ thresholds, rich structure from 5d/5f interaction similar to the $4d^9 5f^{n+1}$ excitations in the RE is observed.

A detailed comparison of the L_3 near edge features in various U compounds is presented in Fig. 2. The WL positions of hexavalent UO_3 and trivalent UCl_3 are shifted by $\approx 2\text{eV}$ and $\approx -4\text{eV}$, respectively, with respect to tetravalent UF_4 or UO_2 , in qualitative agreement with expectations of more efficient core-hole screening at higher 5f occupation. Note the shoulder $\approx 9\text{eV}$ above the WL maximum in the spectrum of UO_3 , which reminds of mixed valence features in the RE. A least squares fit analysis by a pair of Lorentzians and arctangent functions similar to that of mixed valent compounds indicates a relative intensity of the satellite feature of 80(20)% and an increase in width by a factor of about three, relative to the WL at lower energy. The shape and relative shifts are reproduced at the M_3 threshold, where hexavalent uranyl-nitrate shows a single WL and also a shift of $\approx 2\text{eV}$ relative to UF_4 . This demonstrates, that the satellite is not generally related to hexavalent U systems, but may indicate multielectron excitations from covalent U-O bonding in UO_3 or a shape resonance. The small chemical shifts of both hexavalent U compounds relative to UF_4 as compared to that of trivalent UCl_3 and the satellite feature in UO_3 point to an extended 5f character, in agreement with theoretical estimates of a 5f count

close to two in the even more ionic UF_6 /6/. For U_3O_8 , where two inequivalent U sites were formally assigned to penta- and hexavalent U oxidation states, a rather broad and asymmetric WL (shifted by $\approx 3\text{eV}$ with respect to UF_4) is observed. This is consistent with the concept of covalent U-O bonds of variable strength. In the metallic systems, the WLs clearly broaden and decrease in amplitude, the effect being most pronounced in α -U metal. In view of the remarkable agreement of one electron band structure based calculations of the RE metal L_3 -edges /7/, the variations in edge shape among the metals are expected to closely track the initial 6d DOS. The unusual chemical shift in UNi_5 relative to UCu_5 is interesting in view of recent PE/BIS results on the $UNi_{5-x}Cu_x$ series, which point to a more itinerant 5f character in the Ni-rich alloys /8/; it may therefore indicate 6d/5f hybridisation effects.

Fig 2: XA at the L_3 thresholds of various metallic and non-metallic U compounds

A more direct insight into the 5f electronic structure is possible from excitations at d thresholds. Fig. 3 presents the $M_{4,5}$ XA spectra of a series of U compounds, together with those of Th and ThO_2 for comparison. Apparently, the shapes are rather similar for all the compounds investigated, including "itinerant" $\alpha\text{-U}$ as well as "localised" UO_2 . To determine finer details of the spectra, a least squares fit analysis was performed, using asymmetric Lorentzians for the WLs and arctangent functions for the edge jumps and convoluting with the experimentally determined rocking curves. The results indicate an increase in the WL widths between ThO_2 (FWHM= 3.5eV at M_5) and UO_2 or UF_4 (FWHM= 4.4eV). Among the metallic U compounds, a decrease in line width by $\approx 1\text{eV}$ is observed at increasing U-U n.n. distance, approaching the value of UF_4 in case of the UCu_5 and UPt_5 alloys. Since electrostatic 3d/5f interaction is expected to be the larger the more localised the 5f states are, this trend cannot be understood from 3d/5f exchange interaction, but rather points to a narrowing of the 5f band from decreasing f-f overlap at larger U-U distances. The relatively small difference in line width between "itinerant" $\alpha\text{-U}$ and "localised" UO_2 contrasts to the $\approx 50\%$ decrease in line width and vanishing of the edge jump observed for the α -to- δ transition in Pu metal, which was assigned to 5f localisation /3/. This

indicates a less dramatic change of the 5f character in the various U compounds as compared in the two Pu phases and might point to some extended character of the 5f states in UO_2 (and UF_4), in agreement with earlier band structure calculations /9/.

The XA spectra of various metallic and non-metallic U compounds and of ThO_2 at the $O_{4,5}$ thresholds are presented in Fig. 4. A close agreement is observed between the the spectral shapes of ThO_2 and LaF_3 /2/, as might be expected from the empty 5f and 4f shell, respectively, in the ground states of the two compounds and large core-hole/5f interaction from intense wave-function overlap. In particular, the two tetravalent U compounds (UF_4 and UO_2) show rich structure from 5d/5f interaction. The spectrum of UO_3 is clearly different from that of ThO_2 , indicating deviations from a (ionic) $5f^0$ configuration which would be expected in the limit of completely localised 5f states. In the metallic U systems, the spectral features are less pronounced, presumably due to the

Fig. 3: XA spectra of U and Th compounds at the $M_{4,5}$ thresholds

more itinerant nature of the 5f states in these compounds. Most striking is the difference in

spectral shape of the two tetravalent U compounds. There is an additional peak $\approx 3.5\text{eV}$ above the giant resonance in UO_2 , which has no counterpart in UF_4 , in spite of identical $5d^9 5f^3$ excitations expected for localised 5f levels in the two compounds. In view of its position $\approx 20\text{eV}$ above the $5d_{5/2}$ threshold, this peak might be related to a multiple scattering resonance of the outgoing photoelectron. Comparable features are observed for UO_2 at the 3d thresholds (see Fig. 3). Alternatively, it may be related to variations in 5f bonding between the two compounds. One might suspect, that relatively weak differences in crystal field interaction of the 5f states in UO_2 and UF_4 can result in pronounced differences for the pattern of dipol allowed transitions probed by XA. Clearly, multiplet calculations of the $5d^9 5f^3$ excited states including crystal field perturbations would be extremely helpful to clarify this point.

IV. CONCLUSIONS

From the L_3 XA spectra of tri- and tetravalent non-metallic U compounds a value of $\approx 4\text{eV}$ is obtained for the $2p/5f$ coulomb interaction and indications are found for extended 5f states in the formally hexavalent U compounds. At the $M_{4,5}$ thresholds, intense white

Fig. 4: XA spectra at the $O_{4,5}$ thresholds

lines demonstrate the more localised (narrow band) character of the 5f states relative to 6d. Variations in line width of $\approx 20\%$ among the metallic systems are consistent with expectations of a narrowing of the 5f band at increasing U-U distance. No multiplet splitting from core-hole/5f exchange interaction is observed at both, the $M_{4,5}$ and $N_{4,5}$ thresholds. This interaction, however, leads to rich structure at the $O_{4,5}$ thresholds, particularly in the non-metallic U compounds investigated. Differences in the $O_{4,5}$ edge shapes of the two tetravalent U compounds UF_4 and UO_2 may reflect extended contributions in the 5f character of these compounds or be due to multiple scattering effects similar to those at the $M_{4,5}$ thresholds.

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