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LOCALIZATION OF 5f STATES IN VARIOUS URANIUM AND THORIUM OXIDES AND GLASSES

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INTRODUCTION

In actinide compounds 5f electrons are in an intermediate localization regime where the 5f correlation energy is of the same order of magnitude as the 5f bandwidth. Therefore uranium compounds have intermediate behaviour between the systems (like rare earth compounds) exhibiting localized electronic properties (e.g. magnetism) and the systems exhibiting delocalized properties (e.g. superconductivity) (1-2). Of particular interest is the question of the localization versus itinerancy of 5f electrons determined by different uranium oxygen bonding configurations, by different crystalline structures and by changing the U-U distance. In oxide compounds, the open questions concern the hybridization of 5f orbitals with the O(2p) or the U(6d,7s) orbitals for various uranium-oxygen bonding configurations (3-4). It is also of present interest to discuss the role of final state effects in core level spectroscopies as compared to their role in photoemission; these effects can be very important for localized states as it has been found in rare earth compounds.

Important structural and electronic changes are observed along the series of UO_{3-x} oxides (0<x<1). UO_2 has been the most studied (5-6). As well as ThO_2 it crystallizes in the fluorite structure with eight-fold uranium coordination. In the range 0<x<0.5 interstitial oxygens enter the distorted "fluorite type" structure forming uranium sites with ten-fold coordination (7). In the range 0.5<x<1 the uranium local structure can be described as formed by distorted pentagonal bipyramids with two short U-O bonds and five oxygens on the
basal plane. In these oxides different sites with different uranium effective charge have been found (8). It is commonly assumed that for uranium coordination number larger than eight 5f orbitals enter more strongly in the chemical bond as it is shown by the decreasing of the intensity of the mostly pure-5f occupied valence band at -1.5eV. We report results for the three oxides, UO2, UO2.25 and UO2.66.

The glasses are borosilicate glasses (60 wt% SiO2, 20 wt% B2O3, 13 wt% Na2O and 7 wt% ThO2 or UO2). Uranium is expected to be mainly in the form of uranyl complexes U6+, which are linear or nearly linear with a very short U-O distance (1.75-1.78Å). An EXAFS study of the thorium and uranium sites in glasses is described in this volume (9). Crystalline uranyl nitrate hexahydrate has been chosen as a model for this uranium bonding.

EXPERIMENTAL

The spectra were recorded by direct transmission at LURE-DCI (Orsay). For the M-edges in the 3-4 keV range the monochromator was a double crystal Si(111). The measurements were made either with the machine running at low energy (1.56 GeV) or using a double flat reflecting mirror to avoid harmonic contamination when the machine was running at 1.72 GeV. The L-edges in the range of 17 keV were measured using a Si(400) "channel-cut" crystal with the machine running at 1.85 GeV. The instrument bandwidths are principally determined by the size of the synchrotron source giving a full width at middle height 0.7 eV for M edges and 5 eV for L edges. The intrinsic core-level widths are reported on the table.

RESULTS

M4 and M5 thresholds are dominated by a "white line" due to transitions from the 3d core level to unoccupied f-states. The strong absorption is due to the atomic resonance in the 3d--5f atomic cross section.

As an example edge spectra of ThO2, UO2, UO2.25 and UO2.66 up to 50 eV above the absorption maximum are reported in Fig.1. In the range 10-50 eV above the absorption maximum the features are mainly determined by multiple scattering effects and therefore by the atomic arrangement (10). The similarity between UO2 and ThO2 spectra is expected since the crystalline structures are the same. The shifts in energy of the maxima a and b going from UO2 to ThO2 are consistent with the M-O=d istance variation according to the (E-E0)d2 = const. formula. The peak b' in the spectrum of UO2.25 can be assigned to ten-fold uranium sites formed by interstitial oxygens. The peak b of UO2.25 which coincides with the peak b of UO2.25 is due to undistorted eight-fold uranium sites. The energy separation between b and b' indicates a contraction of about 5% of the nearest U-O distance in the ten-fold sites.

This is in agreement with crystallographic results. The widths of the white lines are always broader than the experimental resolution convoluted by the core level width. The widths and shapes are very different in different compounds and that contrasts with rare earth compounds where the widths of transitions from core states to unoccupied atomic-like 4f-states are nearly constant.

Except for thorium in glass, the peaks are strongly asymmetric as shown in the table where the half widths in the low and in the high energy sides are reported separately.
The asymmetries are however smaller in these oxide compounds than those observed in uranium intermetallic compounds by Lawrence et al. (2). In fig. 2a we report the M₄ white lines of thorium in the borosilicate glass and in ThO₂. The final states are 3d 5f₁ and no multiplets could be present.

<table>
<thead>
<tr>
<th>Core level half-width</th>
<th>Absorption peaks half-widths</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thglass</td>
</tr>
<tr>
<td>M₄</td>
<td>1.9</td>
</tr>
<tr>
<td>(3d3/2)</td>
<td>1.6</td>
</tr>
<tr>
<td>M₅</td>
<td>3</td>
</tr>
<tr>
<td>(3d5/2)</td>
<td>1.6</td>
</tr>
<tr>
<td>L₃</td>
<td>6.6</td>
</tr>
</tbody>
</table>

(Γ₁ = half width at middle height in the low energy side, Γ₂ in the high energy side). All energies in eV.

No shift of the energy position of the thorium white line is observed going from the crystalline oxide to the glass. It is symmetric in the glass and its half width is only 1.9eV. An intrinsic width of 1eV for unoccupied 5f states can be deduced. In crystalline ThO₂ the half width Γ₁ increases to 2.8eV showing an increase of 1eV of the 5f localized unoccupied band width and the white line becomes strongly asymmetric. This indicates that in the glass, the unoccupied 5f-states are confined in a narrow band, being localized at least at molecular level in the cluster formed by the thorium atom and its first oxygen neighbors. On the contrary 5f unoccupied states form a broad band in the crystalline oxide (1eV in the glass and 5-6eV in the crystal). The main difference is the long tail on the high energy site for the crystalline oxide which indicates that the 5f orbitals contribute to the mainly (6d,7s) conduction band extending at higher energy up to 12eV.

Same comparisons are reported for the uranium compounds in fig. 2b, c. Things are more complicated for uranium than for thorium since the oxidation number, and 5f-occupation, is not unique. The white line is narrower and more symmetrical in the glass than in any crystalline compound though a small asymmetry is present which does not exist in the thorium-containing glass.
The energy position of the M4,5 white line moves from the energy position in UO2 towards higher energy in hyperstoichiometric oxides increasing by 0.8+0.2eV in UO2.25 and by 1+0.2eV in UO2.66 in uranyl nitrate and in the glass (Fig.25). This shift is similar to the 1.1+0.5eV measured for core level shift in XPS spectra going from formal U(VI) to U(IV) ions in oxides. χ increases from 2.5 to 3eV going from the glass to UO2 and the line becomes more asymmetric. The M4,5 absorption peaks of crystalline uranyl nitrate and of uranium in the glass have the same widths in the low energy side. They are likely to be due to 3d 5f1 final states. The narrow bandwidth of unoccupied 5f states indicates that they are well localized as they are in the thorium containing glass. On the contrary the 5f band is broader and very asymmetric in UO2, UO2.25 and UO2.66. The M4,5 spectra of crystalline uranyl nitrate exhibit a shoulder at about 3.5+4eV above the absorption maximum which is not present in glasses. Following the above discussion we assign this shoulder to the f-components of the U(6d,7s) conduction band. The characteristic spectrum of uranyl is determined by the fact that the unoccupied 5f-states are more localized than in uranium oxides and appear separated from the U6d conduction band. However an important hybridization between U(5f) and U(6d,7s) orbitals is present as indicated by theoretical calculations which show also a large mixing of U5f and O2p orbitals. The non-bonding occupied states of almost pure 5f character, which are at -1.5eV in UO2, are not present in the valence band spectra of uranyl compounds. The optical spectrum of uranyl nitrate does not reveal f--f transitions and shows a charge transfer gap at about 3eV that can be assigned to the transition from the mostly O2p band to the unoccupied U5f states. Therefore the hypothesis that the shoulder at 4eV at the M4-edge is due to a charge transfer excitation of a valence electron should be discussed. The charge transfer gap (O2p--U5f)=3eV is close to the U5f correlation energy (2eV). A mixing of the localized configurations 5f0 and 5f1L can be expected as in CeO2 and NdO that we call interatomic intermediate valence systems. Where this hypothesis will be verified the 4eV satellite in the M4-XANES can be associated with the final state 3d−(6,c)d resonance in the atomic cross section. We have subtracted in each spectrum an arctan curve which simulate the atomic absorption jump. The resulting signals are reported in Fig.3b. M3 spectra have been recorded and are very similar since the smaller experimental broadening is counterbalanced by the large core-level width (though smaller than the predicted value). A single line is observed in UO2. The L3 (and M3) spectra of uranium in the uranyl nitrate and in UO2.66 show a broad multiple scattering resonance (MSR) at 10eV and 15.3eV above the absorption maximum respectively.
The energy positions of these MSR features have been determined by fitting with a second broad lorentzian curve. In the case of uranyl compounds it has been shown by angular-resolved measurements that the MSR is determined by multiple scattering in the direction of the linear U-O-U group (11). In UO2 the MSR seems characteristic of the pentagonal bipyramid group. The presence of these MSR in spectra of glasses bring direct information about the uranium sites.

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