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Abstract
Resonant x-ray scattering spectra of UO_3 were measured at the U M_5 edge using
monochromatic photon excitation. Large differences in inelastic scattering
profiles were observed between two 90°-scattering geometries with the
polarization vector of incident synchrotron radiation parallel and perpendicular
to the scattering plane, respectively. For the latter case, a ∼9.5 eV energy-loss
structure, associated with the O 2p → U 5f charge-transfer satellite, shows a
significant intensity enhancement. The observed resonance behaviour allows
an accurate estimation of the energy of this satellite, which is obscured in the
other experimental geometry, and indicates the charge-transfer origin of the
U M_5 absorption structures at the respective excitation energies.

1. Introduction

Recent successes of resonant inelastic x-ray scattering spectroscopy (RIXS) in probing the
electronic structure of correlated materials, including lanthanide and actinide systems (see, for
instance, the recent review [1]), allow us to consider this technique as one of the important
emerging tools in the field of solid-state physics. This came about as a result of the construction
and further development, within the few last years, of high-brilliance synchrotron radiation
sources, which provide access to tunable monochromatic photon excitation, as well as high-
resolution spectrometers. Tunable excitation gives researchers the opportunity to characterize
the ground and specific excited electronic states due to the site and symmetry selectivity of
the RIXS technique (the technique has also been called resonant x-ray Raman or resonant

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x-ray fluorescence spectroscopy). In particular, the problem of charge-transfer processes can be successfully addressed [2, 3].

Furthermore, synchrotron radiation has the important characteristic of being linearly polarized. From the basic principles of RIXS it is clear that one could obtain rather rich information from RIXS by taking advantage of the polarization properties. This has been recently emphasized by both theoretical and experimental results for early transition metal compounds reported in [4] and [5], where the charge-transfer excitations were studied using different scattering geometries. Strong variations of intensity in ligand $2p \rightarrow$ metal $3d$ charge-transfer satellites were observed in RIXS spectra at the metal $2p$ edge, depending on the relative orientation of the incident and scattered light. The observed spectroscopic behaviour was explained well within the framework of an Anderson impurity model, thus providing insight into the driving mechanisms of the ground-state properties and the physical quantities involved in the systems studied. As regards the strong dependence of RIXS on scattering geometry [4, 5], it is of interest to perform similar studies on so-called mixed-valence compounds containing f elements, where the ligand 2p–metal f charge transfer plays an important role and the ground state can be described as a mixture of several electronic configurations. One such compound is UO_3 [2, 6–9], which can serve as a good model system.

Oxygen-containing compounds of hexavalent uranium often contain inequivalent U–O bonds. Two different types of U–O bonding are found in orthorhombic γ-UO_3, with D_{2h} symmetry at the U site [10, 11]. Having six nearest O neighbours, a uranium atom forms short axial oxygen bonds ($\sim$1.79 Å) and longer bonds ($\sim$2.30 Å) with O in the equatorial plane. The inequivalence of the oxygen sites can cause changes in the degree of U 5f–O 2p hybridization since it is expected to scale with the cation–anion distance [12]. The charge-transfer energy may also be different for inequivalent U–O bonds in γ-UO_3. These differences may lead to a larger energy and intensity spread of the charge-transfer structures, thus making them obscure in x-ray absorption and core-level photoemission spectra. The site selectivity and the resonance behaviour of charge-transfer satellites in RIXS spectra make the RIXS technique an attractive technique to employ in such situations.

In this paper we present the results of a RIXS study of γ-UO_3 at the U M_5 edge. The primary focus is on the influence of experimental scattering geometry on the RIXS spectra of this oxide. The potential of RIXS spectroscopy to probe the charge-transfer phenomena in the system with strong metal 5f–ligand 2p hybridization is discussed on the basis of an examination of the differences between the data obtained from the two experimental geometries and the origin of those differences.

2. Experimental details

The γ-UO_3 sample was a bulk pressed pellet from 99.8% material obtained from Alpha Aesar (Ward Hill, MA, USA) and was affixed to a stainless steel sample holder. The x-ray absorption and scattering measurements at the U M_5 edge of this oxide were performed at bending-magnet beamline X24A of NSLS, Brookhaven, using a double-crystal monochromator equipped with Si(111) crystals [13]. The resolution of the monochromator was about 0.5 eV. The absorption spectra were measured at normal incidence using the total-electron-yield (TEY) mode. RIXS spectra were obtained using a fluorescence spectrometer based on a bent Si(111) crystal and a position-sensitive proportional detector [14]. The total resolution, estimated from the full width at half-maximum of the elastic peak, was $\sim$1.4 eV. To minimize self-absorption effects for UO_3, the incident beam was oriented at approximately $20°$ from the sample surface (or $70°$ from the normal).
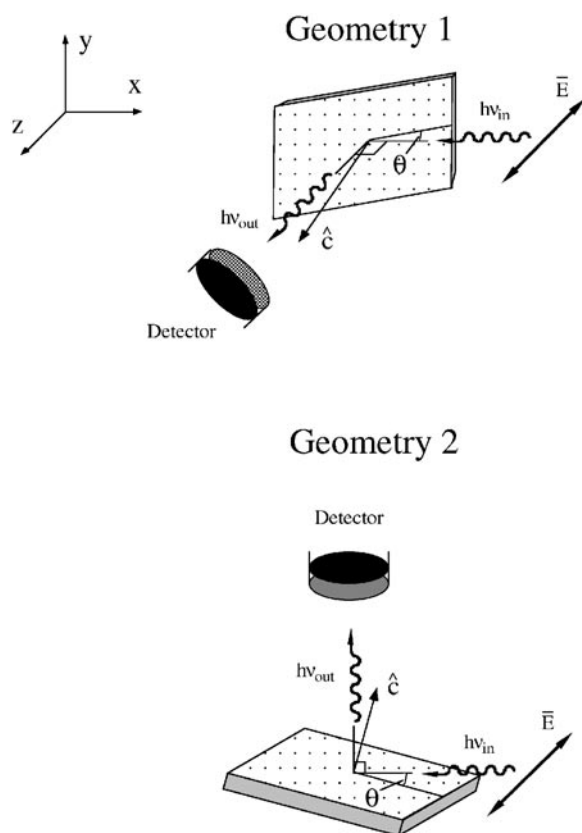
Figure 1. Experimental geometries used for the RIXS detection for UO$_3$. The *c*-axis indicates the sample surface normal.

The two different scattering geometries used in these experiments are shown in figure 1. In both cases the scattering plane was normal to the sample surface and the scattering angle between the incident and scattered photons was fixed at 90°. This was achieved by rotating the fluorescence spectrometer from the horizontal to the vertical position. Thus, for horizontal (*Geometry 1*) and vertical (*Geometry 2*) detection of the scattered x-rays, the polarization vector of incident photons was parallel and perpendicular to the scattering plane, respectively.

3. Results and discussion

The upper panel of figure 2 displays the inelastic part of the x-ray scattering spectra of UO$_3$ recorded at various excitation energies throughout the U M$_5$ edge for both horizontal-detection (dots) and vertical-detection (solid curves) geometries. The spectra are plotted on an energy-loss scale, so the line at 0 eV corresponds to the elastic peak. The letters a to f correspond to excitation energies indicated by arrows on the TEY spectrum that is displayed in the lower panel of figure 2. The spectra mainly reflect 3d$_{5/2}$–5f radiative transitions, because the contribution from the 3d$_{5/2}$–7p transition is expected to be negligible.

The TEY spectrum of UO$_3$ exhibits fine structure that is situated at around 3.5 and 9.5 eV above the main maximum. Similar structures were observed for another hexavalent uranium
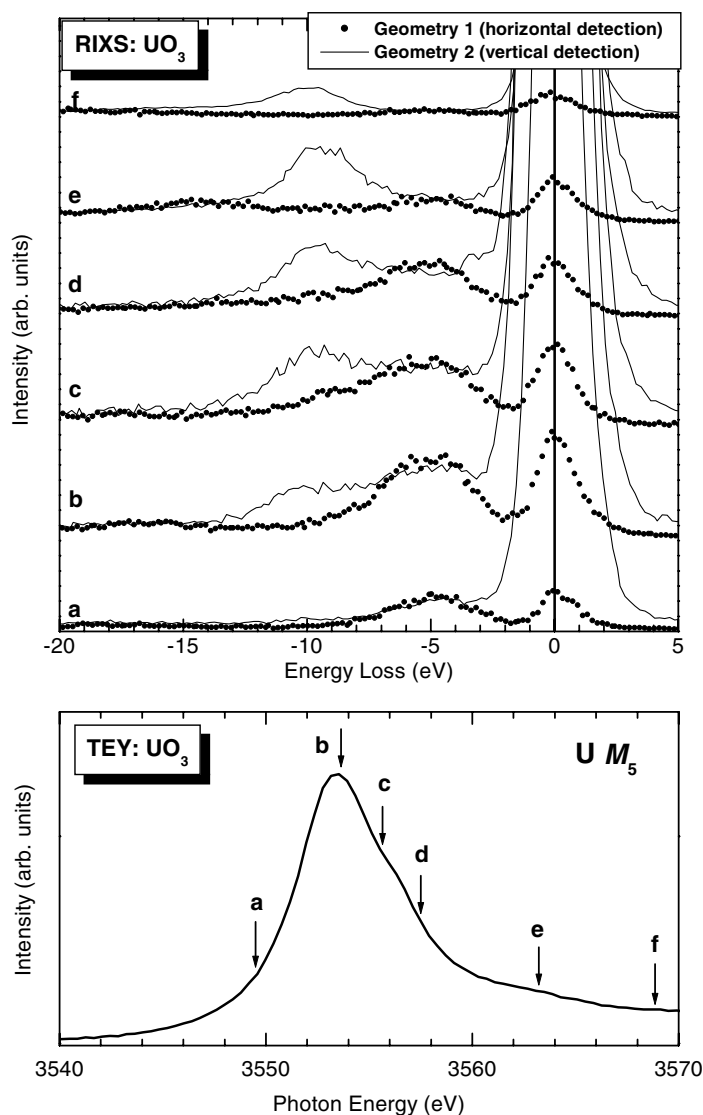
Figure 2. Upper panel: RIXS of UO₃ recorded for different experimental geometries at a number of excitation energies across the U M₅ edge; lower panel: the TEY spectrum of UO₃ at the U M₅ edge. Lettered arrows on the TEY spectrum indicate the excitation energies.

compound, uranyl nitrate, and were suggested to represent a charge-transfer satellite and a multiple resonance scattering, respectively [15]. However, it is difficult to unambiguously confirm these assignments from absorption alone. The reason for these difficulties is that the absorption spectrum is significantly broadened due to the short lifetime (3.2–3.4 eV) of the U $3d_{5/2}$ core hole [16–19]. However, the resolution of the RIXS spectra is mainly determined by the resolving power of spectrometer. Therefore, the RIXS technique is potentially more useful for probing charge-transfer processes in these situations.

An inspection of figure 2 shows that in *Geometry 2* the elastic peak is greatly enhanced in x-ray scattering spectra of UO₃ while in *Geometry 1* it has relatively low intensity. The inelastic structures in the energy-loss region around 5 eV are present for the both sets of spectra, while

the structure at the energy loss of $\sim$9.5 eV is strongly enhanced only in the spectra recorded in *Geometry 2*. In addition, this structure smoothly resonates and has the maximum relative intensity in spectrum e, *Geometry 2*, when the incident photon energy is tuned to the $\sim$9.5 eV structure in the TEY spectrum of UO_3. The observed spectral behaviour can be tentatively explained on the basis of considerations similar to those put forward in [4, 5, 20] for early transition metal and rare-earth systems using the Anderson impurity model.

According to this model, the ground state of strongly covalent UO_3 can be described as a mixture of a few electronic configurations, namely $5f^0$, $5f^1\underline{L}$ and $5f^2\underline{L}^2$ (here $\underline{L}$ denotes the hole in the O 2p band). Since RIXS transitions to states of predominantly $5f^2\underline{L}^2$ character are relatively weak in recorded spectra, we will discuss the spectral structures in terms of coupling only between $5f^0$ and $5f^1\underline{L}$ configurations, for simplicity. This indicates that the elastic peak reflects a transition to a bonding state, whereas inelastic structures at around 5 and 9.5 eV represent transitions to nonbonding and antibonding states, between $5f^0$ and $5f^1\underline{L}$ configurations, respectively. Bonding and antibonding states have $J = 0$ character, with the nonbonding component representing states of the $5f^1\underline{L}$ configuration with other J-values. The transitions to these states become allowed due to their coupling with the $J = 0$ irreducible representation of the $5f^1\underline{L}$ configuration and via the excitation–de-excitation process via an intermediate state.

As discussed in [20], the cross-section for scattering to the states with $J = 0$ is expected to be zero for linearly polarized incident x-rays with their polarization vector parallel to the direction of the scattered photons (i.e., 90° scattering angle). This means that the scattering transitions to the bonding and antibonding states are forbidden for *Geometry 1*, but become allowed for *Geometry 2*. Transitions to the nonbonding states can be observed for both geometries. However, contrary to theoretical predictions [20], both the elastic (recombination) peak and 9.5 eV satellite are still present in a set of RIXS spectra recorded in *Geometry 1* (figure 2) although the intensity ratio for the elastic peak between the two geometries is greater than 100. One of the reasons for this may be that the incident photon beam was not completely p-polarized. A comparison of data from the two scattering geometries suggests that even a small contribution from geometries of s-polarized light may produce a sizable intensity effect in the elastic peak and 9.5 eV satellite. Another possible contributing factor could be a slight misalignment of the spectrometer relative to the incident photon beam such that the scattering angle was not equal to exactly 90° and/or the polarization vector is slightly out of the scattering plane.

For *Geometry 1* similar RIXS data on UO_3 were published in a previous study [2]. Although, the presence of the charge-transfer satellite as an antibonding combination between $5f^0$ and $5f^1\underline{L}$ configurations was pointed out, it was difficult to accurately establish its energy because a distinct resonance of this satellite was lacking. Here, the use of another scattering geometry with the polarization vector of incident photons perpendicular to the scattering plane allowed more accurate determination of the energy of the charge-transfer satellite in the RIXS spectra of UO_3. This satellite, appearing at an energy loss of about 9.5 eV, resonates at the excitation energy $\sim$3563 eV, suggesting that the absorption structure $\sim$9.5 eV above the main absorption maximum of the U M_5 edge also has a charge-transfer origin and could be considered as an antibonding counterpart for $3d^95f^1$ and $3d^95f^2\underline{L}$ configurations in the TEY spectrum. Both the $\sim$9.5 eV scattering and absorption satellites probably result from 5f hybridization of the uranium atom with the 2p states of two axial oxygen atoms. The resonance of the charge-transfer satellite in RIXS spectra of UO_3 is not as sharp as that observed for TiO_2 [4,5]. The reason for this is the much shorter lifetime of the U $3d_{5/2}$ core hole. A large core-hole lifetime broadening gives rise to spectral weight transfer from the antibonding to the bonding component for the configuration interaction in RIXS spectra, as discussed in [21].

4. Summary

The RIXS of γ-UO$_3$ has been studied. The polarization of the incident photon beam was taken into account by performing the experiment in two different scattering geometries. The results obtained are consistent with theoretical considerations reported in [5, 20]. The utility of the RIXS technique for probing the O 2p $\rightarrow$ U 5f charge-transfer excitations in UO$_3$ was demonstrated. The scattering geometry with the polarization vector of the incident x-rays perpendicular to the scattering plane was found to be optimal for observing the intense charge-transfer satellites and determining their energies in actinide systems.

Acknowledgments

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