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Invisible structures in the X-ray absorption spectra of actinides

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ABSTRACT

The X-ray absorption spectra of actinides are discussed with an emphasis on the fundamental effects that influence their spectral shape, including atomic multiplet theory, charge transfer theory and crystal field theory. Many actinide spectra consist of a single peak and it is shown that the use of resonant inelastic X-ray emission spectra (RIXS) has the potential to reveal many new features in the X-ray absorption spectra of actinides. The new range of RIXS beamlines will allow the determination of new structures in the X-ray absorption spectra that have been hitherto invisible. This has the potential to become an important tool in the determination of the electronic structure of actinides.

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1. Introduction

This paper discusses some fundamental aspects of the X-ray absorption spectra (XAS) of actinides. The focus is on the general aspects that influence the spectral shape. Details on specific actinide systems, for example the heavy fermion systems, are not included. A detailed review of the spectroscopy of the 5f states in actinides has been recently published by Moore and van der Laan [1].

The central aspect of the electronic structure of an actinide is the partly filled 5f band. The 5f electrons are more delocalized than the rare earth 4f electrons, but less delocalized as the d-electrons of the 3d, 4d and 5d transition metal systems. Because of the relatively strong localization of the 5f electrons, the atomic interactions are important if one excited a core electron. As an indicator for the atomicity of an orbital we use the cubic crystal field strength (10Dq) as a measure. The crystal field strength is a measure of the splitting of 4f, 5f and 3d states due to the inhomogeneity of the surroundings, for example an octahedral symmetry. Typical crystal field strengths for oxides are 0.03 eV for 4f systems, 0.25 eV for 5f systems and 1.5 eV for 3d systems. In other words a 4f state is approximately 5 times more localized than a 5f electron and a 3d electron is ~5 times less localized. As such one would expect the general behavior of 5f electrons to be intermediate between 4f and 3d systems.

2. Atomic aspects in 5d XAS spectra

The 5d XAS spectra of uranium and other actinides are dominated by many peaks and structures related to multiplet effects. In contrast, all other XAS spectra (4d, 3d, 2p) do show only a single peak that does not seem to contain fine structure. We explain the atomic features of the actinides by its 5d XAS spectrum, which has the strongest coupling between the core state and the 5f states. The main features of the 5d XAS spectra of actinide systems can be described with an isolated atom or ion. This allows us to explain some of the fundamental issues concerning 5d5f ($O_{4,5}$) edges, in particular the importance of 5f5f intra-atomic interactions and the 5f spin-orbit coupling.

X-ray absorption spectra of free atoms can be described with atomic multiplet theory. The atomic Hamiltonian is usually divided into large energy terms consisting of the kinetic energy, the nuclear energy and the spherical averaged electron–electron interaction. Together these three interactions determine the energy of a certain configuration. The remaining two smaller energy effects, i.e. the non-spherical electron–electron interaction and the spin–orbit coupling determine the splitting of the states (indicated with term symbols) within a certain electron configuration. This splitting of a certain $5f^n$ configuration is indicated as multiplet splitting. The ground state is given by the Hunds rules, i.e. (1) maximum S, (2) maximum L and (3) maximum J, if the shell is more than half-full. An isolated U^{4+} ion has an electronic configuration $5f^2$. The ground state configuration of the two 5f electrons is given by the Hunds rule, which yields a ground state with $L=5$ and $S=1$, represented by a 3H term symbol. The 3H state is split into three substates by the 5f spin-orbit coupling and the ground state has 3H_4 symmetry. The 5f spin-orbit coupling is 0.26 eV, too large to be affected

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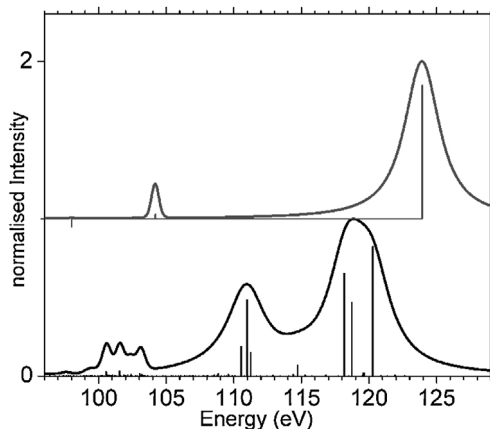


Fig. 1. Atomic multiplet calculations for the 5d5f transition of $5f^2 U^{4+}$ (bottom) and $5f^0 U^{6+}$ (top). The $O_{4,5}$ edge is spread over 20 eV due to large 5d5f and 5f5f multiplet effects. The broadened spectra use a broadening that cannot be achieved with normal 5d XAS experiments to highlight the potentially observable spectral features.

by temperature effects. Fig. 1 shows the 5d X-ray absorption spectrum that can be calculated by performing an atomic multiplet calculation of the final state in which a 5d electron has been excited to a 5f state, which corresponds to a $5d^9 5f^3$ configuration. The 5d spin-orbit coupling is relatively small (3.2 eV) and the O_4 and O_5 edges overlap in energy. The 5d5f multiplet interaction, in other words the higher order interaction of the electron–electron repulsion term coupling the 5d and 5f electronic states is large ($F^2 = 10.6$ eV), resulting in a combined $O_{4,5}$ multiplet spectrum that spreads over 20 eV. For more details regarding the use of atomic multiplet theory in X-ray absorption spectroscopy, we refer to *The Theory of Atomic Structure and Spectra* [2], the *Hitchhiker's guide to multiplet calculations* [3] and *Core Level Spectroscopy of Solids* [4].

3. Other X-ray absorption spectra of uranium

UO_2 and UF_4 have a $5f^2$ ground state. Fig. 2 shows its L_3 edge ($2p_{3/2} \rightarrow 6d$) at $\sim 17,180$ eV, M_3 edge ($3p_{3/2} \rightarrow 6d$) at ~ 4310 eV, M_5 edge ($3d_{5/2} \rightarrow 5f$) at ~ 3550 eV and N_5 edge ($4d_{5/2} \rightarrow 5f$) at ~ 730 eV show essentially a single peak at the edge, followed by additional structure at higher energy. These X-ray absorption spectra taken over a larger energy range should correspond closely to single particle calculations. The resolution of the spectra does not allow any detailed multiplet analysis of the edge structure. As discussed above, only the $O_{4,5}$ spectrum ($5d \rightarrow 5f$) at ~ 100 eV shows significant fine structure, related to the $5d^9 5f^3$ final state multiplet. The $5d^9 5f^n$ multiplet spectrum is similar to the $4d^9 4f^n$ multiplet for the rare earths, with a series of small pre-edge peaks followed by a large absorption peak [5]. In contrast the 4d XAS spectrum ($N_{4,5}$ edges) seem to show only a single Lorentzian peak. The reason that only a single peak is visible is the large lifetime broadening of approximately 6 eV [6].

Fig. 3 shows the atomic multiplet calculation of the 4d XAS spectrum, where only the $4d_{5/2}$ (N_4) edge is shown. If one could lower the lifetime broadening to 0.5 eV, one would observe clear fine structure due to atomic multiplet effects. The $4d_{7/2}$ (N_5) edge has less fine structure than the N_4 edge and is not shown. It will be shown below how such fine structure could be made visible.

4. The screening of the core hole: charge transfer effects

The theory of X-ray spectroscopy of open shell systems is based on the charge transfer model, as introduced by Kotani and Toyozawa [7]. The charge transfer method is based on the Anderson

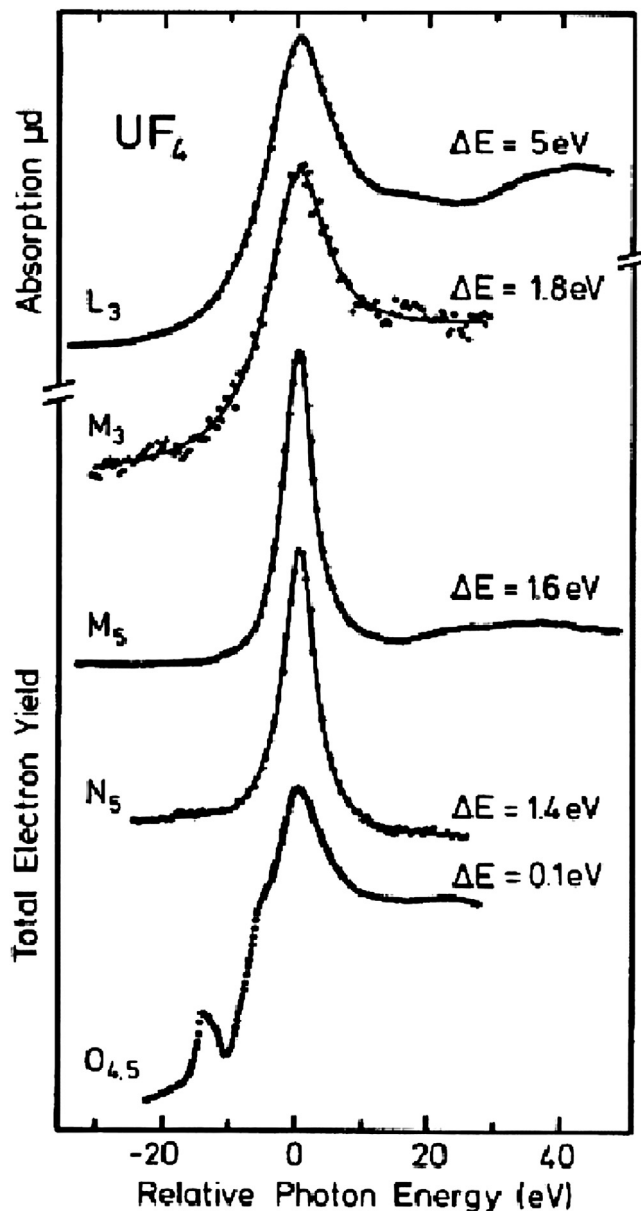


Fig. 2. The L_3 , M_3 , M_5 , N_5 and $O_{4,5}$ edges of UF_4 . Reprinted from [4].

impurity model and describes a localized state, the $5f^n$ state, which interacts with delocalized electrons in bands. One can combine this configuration with other low-lying configurations similar to the way configuration-interaction works. The charge-transfer model adds a configuration $5f^{n+1}\underline{L}$ to the $5f^n$ ground state. In the case of an actinide oxide, in a $5f^{n+1}\underline{L}$ configuration an electron has been moved from the oxygen 2p valence band to the actinide 5f band and the \underline{L} represents a ligand hole. The energy difference between the $5f^n$ and $5f^{n+1}\underline{L}$ configurations is defined as the charge-transfer energy.

The effects of charge transfer are particularly apparent in the 4f XPS spectra of actinides [8]. In case of 4f XPS the ground state of U^{4+} can be described $5f^2 + 5f^3\underline{L}$ and the final state as $4f^{13} 5f^2 \varepsilon + 4f^{13} 5f^3 \underline{L} \varepsilon$. In the XPS final state, the 4f core hole modifies the ordering of the 5f configurations and the final state with the lowest energy will change from $5f^2$ to $5f^3$. Charge transfer multiplet calculations can take care of these effects in detail as explained by Kotani and Ogasawara [8]. It is important to note the large difference between XPS and XAS in this respect. XPS of open shell systems is often

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