Electronic structure of oxide fuels from experiment and first principles calculations

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Abstract. Energy loss spectra from a variety of cubic oxides are compared with ab-initio calculations based on the density functional plane wave method (CASTEP). In order to obtain agreement between experimental and theoretical spectra, unique material specific considerations were taken into account. The spectra were calculated using various approximations to describe core-hole effects and electron correlation. The calculations are based on both the generalized gradient approach and the local spin density approximation when dealing with the correlation in to show qualitative agreement with the sensitive oxygen K-edge spectra in ceria, zirconia, and urania. Comparison of experimental and theoretical results let us characterize the main electronic interactions responsible for both the electronic structure and the resulting EELS spectra of the compounds in question.

Introduction

In the past few years, there have been growing efforts to apply modern first principles materials modelling tools as a framework for accelerated materials design and development. One area where such modelling efforts can make unique contributions is in the understanding of the evolution of the mechanical properties of advanced nuclear fuels (key to many future reactor designs). Establishing a damage evolution model for oxide fuels currently suffers from inaccurate models where there is lack of data due to a lack of experimental studies. As damage mechanisms need to be extrapolated for the expected 50 year lifetimes of reactors, the absence of models that accurately address the energetic contributions of all the induced defects limits the applicability of the theoretical models. Direct validation of the theoretical techniques, in their application to oxides, requires direct experimental measurements of structure, composition and electronic interactions at the nanometer scale – in

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particular to observe the atomic and electronic structure of relevant point defects and their extended complexes. Model validation can be achieved by acquiring images and an electron energy loss spectrum (EELS) in a scanning transmission electron microscope (STEM). As we are interested in oxide fuels, the oxygen $K$-edge is chosen to compare experiment and theory directly, and here we attempt a first validation of the theory by studying three fluorite structured oxides - ceria, zirconia, and urania. Within the density functional theoretical framework we employ a variety of calculations, but for the purposes of this presentation both the generalized gradient (GGA) and local spin density approximation (LSDA+U) with unique materials considerations using the CASTEP code is considered. The materials considerations include correlated f-states, magnetic ordering, and in view of the direct comparison to STEM/EELS the core-hole effect.

Methods

1.1. Experimental Analysis

Standard ceria, zirconia, and urania powder samples were dispersed on 3 mm standard holey carbon TEM grids. The experimental spectra were obtained from the double corrected FEI Titan at Lawrence Livermore National Laboratory (LLNL) operating in STEM mode at 300 keV. EELS spectra were obtained with a Gatan Tridiem electron energy loss image filter. The energy resolution is 0.7 eV based on the full width half maximum of the zero-loss peak. The acquisition time for each spectrum is 5 seconds with 0.1 eV/pixel dispersion.

1.2. Theoretical Treatment

All calculations presented below are carried out using the CASTEP code [1,2]. CASTEP uses a plane wave basis set and pseudopotentials within the density functional theory formalism. Perdew, Burke, and Erzenhof (PBE) version of the generalized gradient approximation (GGA) was used to describe ceria and zirconia. To describe localized f-orbitals of U, in urania we employed the LSDA+U approach [3] with an effective Hubbard U value of 6 eV to achieve an antiferromagnetic state. Ultrasoft pseudopotentials were generated using the “on the fly” formalism in CASTEP, and one core electron was removed from a relevant core level when performing core–hole calculations [4]. All core–hole calculations were carried out using supercells sufficiently large to eliminate unphysical interactions between periodic images. Previous experience from all-electron calculations gives 8–10 Å as a recommended distance between periodic images. The supercells used in the current study corresponded to the distances between atoms with core holes of 10.822, 10.14, and 10.94 Å for ceria, zirconia, and urania respectively. Crystal symmetry is reduced when a core-hole is introduced in a supercell. All calculations were carried out by using reduced symmetry rather than by ignoring point group symmetry altogether; even a reduced symmetry allows calculation speed to be increased by considering only $k$-points in the irreducible part of the Brillouin zone. All calculations furthermore show a converged antiferromagnetic ground state.

Results

Normalized measured electron energy loss oxygen $K$-edge spectra in ceria, zirconia, and uranium dioxide are compared below with the theoretically predicted spectra from the CASTEP code. All spectra were aligned based on the position of the first experimental peak.
Figure 1. Oxygen K-edge spectra for ceria (a), zirconia (b) and urania (c). Experiment (dots) is compared to CASTEP calculations with (solid line) and without the core-hole effect (dashed line).

Discussion

Building in complexity we have examined the electronic structure of non-correlated and correlated fluorites. When treated correctly across these fluorites structures we predict insulating ground state as confirmed by the analysis of their density of states. EELS K-edge spectra that incorporate information about oxygen partial density of p-states and an energy dependent matrix element were calculated for three transition metal oxides. The resultant spectra were broadened with a Gaussian (width of 0.8 eV for ZrO$_2$ and CeO$_2$, and 1 eV for UO$_2$) to simulate experimental resolution. Across the fluorite oxides, we compare calculated and experimental spectra to quantify the effect of taking core hole into account.

The calculated spectra of ceria, zirconia, and urania show broad agreement with the experiment with or without the core-hole effect. Taking into account the core hole shows a marginally better agreement in some cases, but it appears to be material specific. The core hole effect is suggested in the literature to increase the qualitative agreement with experiment by taking into account the fundamental electronic excitation from 1s to a p-like state [5]. The theoretical spectrum for ceria overestimates the first peak intensity unless core hole effect is taken into account (Figure 1a). In the zirconia case, the near edge region of the spectrum remains largely unchanged by the incorporation of the core hole effect, but the post peak around 550 eV shows better agreement with experiment when the core hole effect is taken into account (Figure 1b). In the correlated urania case, the core hole effect broadens the first peak and post edge peak to show increased agreement with experiment (Figure 1c). However, in all cases, even calculations without the core hole effect produce correct peak positions and qualitatively correct spectra compared with the experimental EELS results.

It is important in electronic structure calculations for correlated materials to use a Hubbard U value that corrects the DFT results sufficiently. In the case of urania the requirement is to predict an insulating ground state, so the correction must open the band gap and tune the overlap between the p and f-partial density of states above the Fermi level. Without a Hubbard U correction for urania, first-
principles calculations predict a metallic ground state [3]. The ongoing issue involves the value of U-J that one must use to predict agreement across a variety of material properties such as band gap and spectra. The U-J value of 6 eV used in this study produces good agreement with the experimental EELS spectrum as demonstrated in Figure 1c. Dudarev et al. used a slightly smaller value of U-J = 4 eV [6]; it appears that either value predicts correct spectroscopic character associated with the oxygen K-edge for urania.

Across the fluorite structures, predicting the electronic structure based on the band structure method in CASTEP shows broad agreement with experiment in terms of peak positions and relative intensities. Incorporation of the core-hole effect has only a marginal effect on the spectroscopic character for the fluorites considered in this study.

Conclusion

The oxygen K-edge EELS spectra for the oxides agree qualitatively with the theoretical electronic structure calculations based on the CASTEP code. Taking into account the core-hole effect shows even better qualitative agreement with experimental EELS spectra. Further theoretical and experimental work will address the influence of structural defects on EELS spectra in these materials.

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