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Probing the Electronic Structure of Transition Metal Oxides using Electron Energy-Loss Spectroscopy

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Electron energy-loss spectroscopy (EELS) carried out in the nano-analytical electron microscope (nano-AEM) is a powerful probe of chemistry, bonding and electronic structure in a wide range of materials. Analysis of energy-loss near-edge structure (ELNES) present on ionization edges in EELS is now recognized as the only technique that can be used to obtain such information with close to atomic-scale spatial resolution. The information on coordination number, local symmetry and oxidation state derived from ELNES data can provide key insights into chemical and structural inhomogeneities in advanced materials. However the electron-specimen interactions that result in ELNES are complex. In order to develop and advance the use of the technique it is important to combine fundamental investigations of the ELNES in known structures with detailed theoretical modeling of the electron-specimen interactions.

This report will focus on the analysis and interpretation of the oxygen K-ELNES in a range of technologically relevant materials. Experimental ELNES data from complex ternary structures such as yttria-stabilized zirconia and ternary oxides with the spinel structure clearly demonstrate that the anion edges can be used to obtain information about BOTH the anion and cation sites. The oxygen K-edges in a range of ternary spinels as the cation the octahedral and tetrahedral site is varied systematically are shown in Figure 1 [1]. Similar results have been obtained in the study of the oxygen K-edge in zirconia powders doped with varying amounts of aliovalent dopants such as Y_2O_3 (Fig. 2) [2]. While it is clear that the oxygen K-ELNES is influenced by altering the electronic structure of neighboring cations the strength of the interaction is not easily predictable – it is a sensitive function of the ion type, the crystallography of the site and local coordination environment.

Previously such data has been interpreted in terms of a fingerprint for the local coordination environment. To go beyond such an interpretation it is necessary to perform electronic structure calculations to model the observed ELNES. Such calculations are an essential step towards a complete interpretation of the experimental data. However, in performing such calculations it is crucial to use a realistic model for the structure under investigation. In the case of Y_2O_3-doped ZrO_2 it is not only crucial to include vacancies and dopant atoms in the model but also to identify the correct atomic positions by permitting lattice relaxations to occur (Fig. 2) [3, 4]. In the case of the ternary spinels the influence of the degree of inversion and the effect of electron correlation on the band structure calculations must be considered (Fig. 3) [5].

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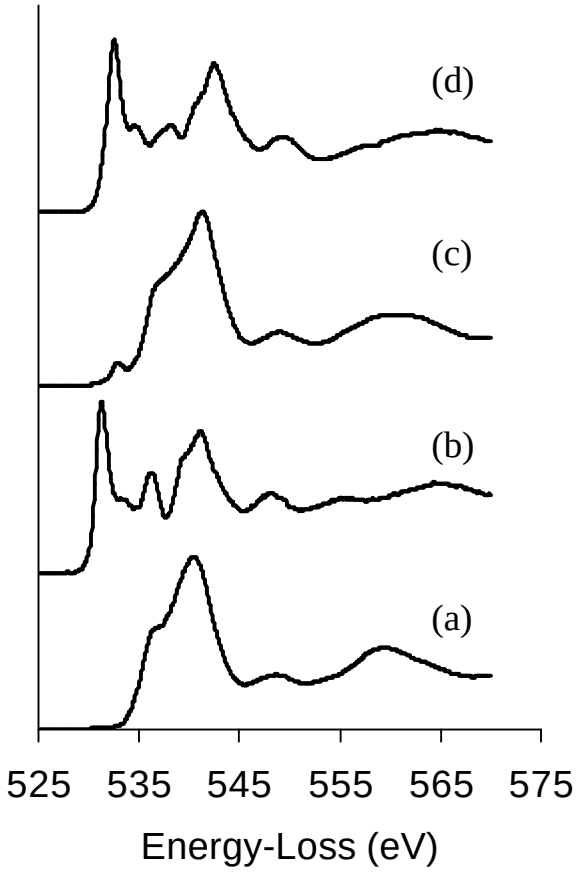

Figure 1. Oxygen K-edge ELNES from (a) $MgAl_2O_4$, (b) $MgCr_2O_4$, (c) $NiAl_2O_4$ and (d) $NiCr_2O_4$ to show the effect of systematically changing the tetrahedral (A-) and octahedral (B-) cations in the AB_2O_4 structure.

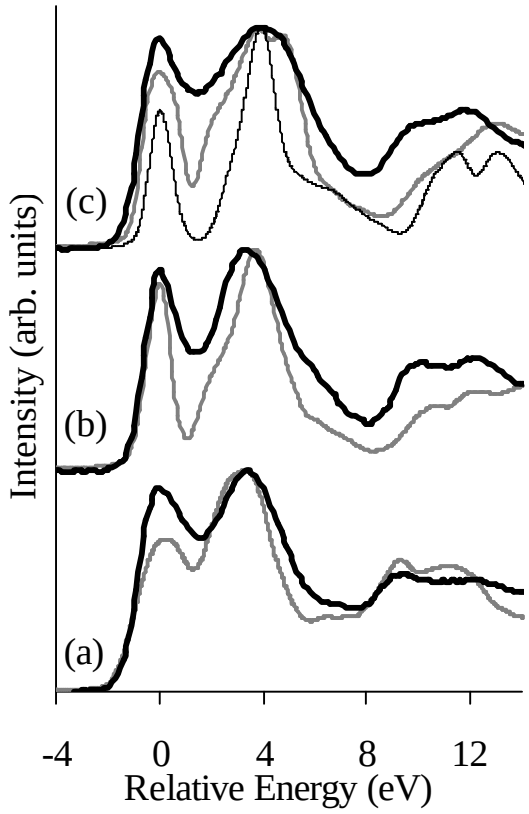

Figure 2. Oxygen K-edge ELNES from (a) pure ZrO_2, (b) 3mol% Y_2O_3-ZrO_2, (c) 10mol% Y_2O_3-ZrO_2. The calculated ELNES obtained after atomic relaxation is shown in each case (grey). In (c) the result of electronic structure calculations without any lattice relaxation is shown (thin black line).

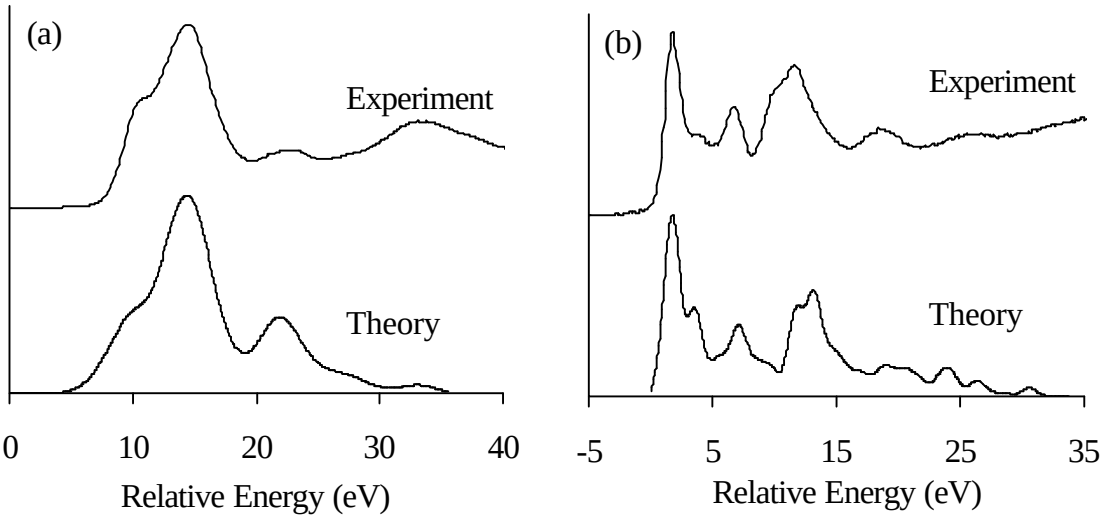

Figure 3. Experimental and theoretical oxygen K-edge ELNES from (a) $MgAl_2O_4$ and (b) $MgCr_2O_4$. Both calculations were performed within the local density approximation but in the case of (b) spin polarisation was required in order to obtain reasonable agreement with experiment.

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