Computational EELS modelling of magnesium oxide systems

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Abstract. An area of contention in ELNES simulations using density functional theory (DFT) has been whether geometry optimisation is entirely necessary to obtain useful results. This issue is addressed for bulk magnesium oxide by comparison of results with and without energy minimisation of structures. An MgO (001) surface was investigated. Experiments were carried out to determine how the predicted oxygen K edges varied in different layers extending from the surface into bulk. Similarly the comparison of the MgO oxygen K edge in bulk and at the interface of Fe(001)/MgO(001) is of interest for spintronic devices. For this system, the oxygen K edge shows pre-edge intensity as compared to bulk MgO, which we attribute to additional states available due to transition metal d / oxygen p orbital interactions at the interface.

1. Introduction
This work considers the energy-loss near edge fine structure (ELNES) for oxygen K edges in various MgO systems. All calculations presented have been carried out using the \textit{ab-initio} density functional theory (DFT) code CASTEP [1].

2. Methodology
In an EELS ionisation event, an electron is promoted from a core-state to a higher lying conduction band. This leaves a 'core-hole' in its place. CASTEP uses a plane wave basis set, and pseudopotentials to approximate exchange and correlation effects. The projector augmented wave (PAW) approach can be used to model core-holes using CASTEP [2-4]. In these experiments, it was considered important to converge the key user-controlled parameters in a DFT code; namely the kinetic energy cut-off and choice of k-point mesh density [5]. A single cell of MgO was constructed in the cubic rock-salt structure (a=b=c = 4.21Å, α=β=γ = 90º), and for one of the oxygen atoms a single electron core-hole was put in place. The oxygen K edge was then converged against the key DFT code parameters. For the kinetic energy cut-off, the value was changed sequentially in 100eV intervals from 300eV to 600eV. Upon each increase, for each data point obtained (on a consistent set of energy axis values) the percentage variation in the edge intensity was found, and those percentage variations were averaged into a single value. The parameter was considered to be converged when the average percentage variation was 1.25% or less. In the EELS section of the calculation, the k-point mesh was increased from 12x12x12 to 48x48x48 in 'steps' of 12x12x12, with the same convergence criterion applied.

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Table 1. Chosen calculation parameters for a single MgO cell with a core-hole in place.

| Parameter                  | Chosen value                                                                 |
|----------------------------|------------------------------------------------------------------------------|
| Kinetic energy cut-off     | 600eV                                                                        |
| EELS calculation k-point mesh | 24 x 24 x 24 (actual spacing – 0.0099Å⁻¹), modified to a spacing of 0.0197Å⁻¹ for surface and interface studies. |
| Core-hole                  | Single electron core-hole in place                                          |

For the subsequent large interface calculations, it was observed that this set of k-points was not computationally practical, so was revised as is explained in Table 1. For bulk MgO the observable differences (when the spectra were plotted) between results correlating to the ‘ideal’ and ‘revised’ set of parameters were negligible.

3. Results

The role of geometry optimisation was considered. The dimensions of a single cell of MgO were systematically varied (with a core-hole in place), and system energies found. The unit cell dimensions that resulted in the lowest system energy were then considered to be ‘geometry optimised’. The resultant unit cell dimensions obtained were $a=b=c = 4.47\text{Å}$, $\alpha=\beta=\gamma = 90^\circ$. In these calculations the electron taken from the core was placed into a conduction state so one might not necessarily expect a contraction of the unit cell. A predicted oxygen K edge was found for this system, and was observed to be at least qualitatively similar to the result for the experimental lattice parameters, though did not display the doublet feature discussed subsequently. Therefore, it was considered acceptable to use experimental lattice parameters in the remaining work. In Figure 1 therefore, a non-geometry optimised single cell result (with a single electron core-hole in place) is compared to experiment [6]:

![Figure 1](image)

The qualitative agreement with experiment is reasonable, especially for the 0.8eV Gaussian-broadened result. The ‘doublet’ nature of the first peak in the spectrum is reproduced for example. Furthermore the theoretical result shows qualitative agreement with Lindner et al’s seminal paper on MgO EELNES [8]. As can further be observed by comparing results a) and b), the ground state result is qualitatively similar to the core-hole result, displaying similar energy separations in terms of the main sets of peaks – though the doublet feature as seen in experiment is not observed. As mentioned previously, this was
also not observed with the geometry optimised result. However, the agreement was considered sufficiently close to use ground state calculations for the surface and interface systems.

For an (001) surface of MgO (with a mixed oxygen and magnesium terminated surface, vacuum thickness 22.7Å), predicted oxygen K edges were found at different positions; at the surface (B), atom (C) (a distance of 4.21Å from a surface) and atom (D) (a distance of 6.32Å from a surface). These calculations were carried out in the ground state. Figure 2 shows the results. As can be observed, by a distance of at most 6.32Å into the surface the result matches that of ‘true’ bulk (on this occasion calculated in the ground state). These results led to an investigation of Fe (001)/MgO(001) interfaces.

Figure 2. a) Standard bulk MgO predicted oxygen K edge, using the revised parameters (see Table 1) in the ground state. b, c and d are atomic positions as labelled. All results are subject to energy-independent broadenings of 0.2eV Lorentzian and 0.4eV Gaussian, aligned by the first peak of spectrum a. Spectra c and d begin to rapidly approach the bulk result. Spectrum b (the surface oxygen result) shows a pre-edge shoulder.

Magnetic tunnel junctions (MTJs) based on Fe/MgO interfaces can act as magnetic sensors or as part of non-volatile memory elements for example [9]. There has been some suggestion in the literature that these interfaces may not be entirely sharp, and a FeO monolayer might form [10,11]. Therefore, one might postulate two possible structures - depicted in Figure 3; a clean interface and an ‘oxidised’ one. Various ground state calculations were performed. Firstly for both structures, deep in the MgO ‘slab’ oxygen K edge predictions were obtained, and it was verified that these matched the simulation for the true bulk result (spectrum a in Figure 2). Indeed, for both the clean and oxidised interfaces (spectra b and c) the MgO ‘slab’ results were a good match for the true bulk result – suggesting a valid construction of the theoretical cells. Therefore, at interface positions 1, 2 and 3 predicted oxygen K edges were found, as are also shown in Figure 3. For results 1-3, there is additional ‘pre-edge’ intensity as compared to bulk. This can be argued to be as a consequence of oxygen 2p / Fe 3d orbital interactions. These interactions will create additional lower-lying unoccupied energy states, hence the ‘pre-edge’ intensity. For the ‘oxidised’ interface structure (spectra 2 and 3), particularly interesting results are observed. As compared to spectrum 1 (for the clean interface), spectra 2 is more ‘bulk-like’ in appearance, but at position/spectra 3, the pre-edge intensity is very high as compared to all the other results.

Experimental results have been added to Figure 3, which have been subject to multi-variate statistical analysis [10-13]. These results are perpendicular line scans of an interface, with 0.3eV energy resolutions obtained at SuperSTEM [14]. The first experimental result is a line scan from the MgO ‘slab’ of the MTJ. As can be observed, this result matches theory reasonably well. The second experimental result is from a line scan at the interface. In this instance the best match (based on
comparison of peak ratios for the pre-edge peak and the first peak in the ‘bulk’ MgO spectrum) is with the predicted result at position ‘1’ of the clean interface. Further work will be carried out on rationalising experimental results for other interfaces, via comparison with theoretical models.

Figure 3. a) Standard bulk MgO predicted oxygen K edge, using the revised parameters (see Table 1) in the ground state. b) The ‘bulk-slab’ result for the clean interface c) is the ‘bulk-slab’ result for the oxidised interface. Spectra 1-3 correspond to the labelled oxygen positions at the Fe/MgO interfaces as shown. All results are shown with a 1.0eV Gaussian broadening. Theoretical results are aligned by the first peak of spectrum a. Experimental results have been aligned relative to the closest matching theoretical results. The experimental results have a 0.3eV energy resolution and have been subject to multivariate statistical analysis [12,13]. Distances: A = 0.149nm, B = 0.235nm, C = 0.224nm [10,11]. For each of the unit cells, a\(=\)b = 0.292nm, c= 3.209nm.

4. Conclusions

Good agreement with experiment was observed for the oxygen K edge in bulk MgO, without geometry optimisation, thus saving significant computational effort. These studies were then extended to an MgO (001) surface. Two possible Fe/MgO interfaces were investigated, predicted results being compared to experiment with reasonable matches obtained – though further work is required.

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