

Band Structures of the Group I and II Oxides: Using EMS Measurements as a Test of Theoretical Models

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Electron Momentum Spectroscopy (EMS) directly measures the band intensities and dispersions of solid targets [1], with no theoretical input required for its analysis. This technique can, therefore, provide results which can be used to test theoretical models of condensed matter. Here we present EMS measurements for the each of the three lightest Group I and Group II oxides, and compare these with Hartree-Fock (HF) and density functional theory (DFT) calculations within the linear combination of atomic orbitals (LCAO) method. These results suggest the need for improvements in the Hamiltonian rather than an increase in basis set size.

1. Introduction

Electronic structure calculations of solids have undergone considerable improvement over the past 40 years and are now at a point where accurate predictions can be obtained for metals and semiconductors. It is difficult to evaluate the success of these calculations when applied to ionic solids due to the lack of experimental data available.

Light alkali and alkaline earth oxides crystallise into simple structures, ie, wurtzite, rock salt or anti-fluorite, with a relatively small number of electrons in their unit cell (maximum of 46 for K₂O). This simplicity makes them ideal for computational studies at the *ab initio* level. EMS can directly measure the band structure of these ionic solids without the difficulties associated with other methods, such as sample charging [2]. Our EMS measurements of the simple oxides provide a comprehensive database of bandgaps and bandwidths which can be used as a benchmark for quantitative assessment of theoretical models.

2. Calculations

We have performed tight binding calculations using the CRYSTAL98 [3] suite of programs at the Hartree-Fock and three density functional levels: local density approximation (LDA) [4], generalised gradient approximation (PBE) [5] and a hybrid method incorporating exact exchange (PBE0) [6]. High quality all electron basis sets optimised for HF were used [7,8,9]. These are presented in Table 1. The calculations were carried out at the experimental lattice parameter [10].

Table 1: All electron basis sets used to describe each ion

Species	Li ⁺	Na ⁺	K ⁺	Be ²⁺	Mg ²⁺	Ca ²⁺	O ²⁻
Basis Set	6-1G	8-511G	86-5116G	5-11G	8-511G	86-511G	8-411G

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3. Results

EMS measures the probability distribution of the target electrons as a function of both energy and momentum. In other words, it measures the electronic structure of the solid as the electron momentum distribution (EMD) of each band combined with the band dispersion. Preparation of the oxide samples (except BeO) is through evaporation of spectroscopic grade metal in an oxygen background on to a thin carbon film. BeO was prepared by repetitive evaporations of a thin layer metal followed heating in an oxygen background. As a result the measured band structure is of a polycrystalline sample. In order for the calculations to be directly compared with the experimental results the theoretical EMDs and band dispersions are ‘multiplied’ together. Calculations are performed over 25 evenly spaced directions and summed together to give spherically averaged data [11]. Finally the calculations are convoluted with gaussians with FWHM of 0.1 a.u. and 1.0 eV to account for experimental resolutions.

Table 2: Valence Bandgaps (O 2p – O 2s) (eV) at the Γ -point energies.

	HF	LDA	PBE	PBE0	Expt.
Li₂O	21.1	15.0	15.2	16.7	16.1
Na₂O	20.2	14.2	14.6	16.0	15.9
BeO	24.9	18.3	18.5	20.2	19.0
MgO	23.1	16.7	17.1	18.7	17.6
CaO	21.2	15.1	15.3	16.8	16.5

Table 3: O 2p Bandwidths (eV). Error in experimental values is ± 0.2 eV.

	HF	LDA	PBE	PBE0	Expt.
Li₂O	2.89	2.12	2.04	2.27	1.3
Na₂O	1.25	1.01	1.02	1.10	0.6
K₂O	0.38	0.37	0.30	0.39	0.3
BeO	6.77	6.43	6.36	6.88	4.7
MgO	4.54	3.61	3.64	3.89	3.3
CaO	2.33	2.28	1.74	2.04	0.9

Table 2 and 3 above demonstrate that the theory reproduces the general trends in the experimental data however, no one theory accurately models these ionic solids.

3.1 Bandgaps

The order of bandgap magnitudes is consistent throughout the six oxides. HF systematically overestimates the bandgap by $\sim 30\%$. LDA systematically underestimates the bandgap but gives better predictions due to the inclusion of electron correlation. The shortcomings of LDA are well known and this underestimation of bandgap is attributed to incomplete cancellation of self-energy terms in the Coulomb and exchange potentials. Modifications to LDA, such as density gradient corrections (PBE) and inclusion of exact exchange (PBE0) produce more accurate valence bandgaps. PBE slightly underestimates the bandgap and PBE0 overestimates the bandgap however, in most cases, provides the best prediction.

3.2 Bandwidths (or Dispersions)

Bandwidths are usually a measure of oxygen-oxygen interaction [12] and therefore would be expected to decrease as the distance between the oxygen atoms increases. This trend is seen in the experimental data as the bandwidths decrease with increasing cation size. It can be also

said that the alkali oxides are more ionic than the alkaline earth oxides with less overlap between neighbouring ions, evidenced by smaller dispersions. EMS-derived bandwidths fall well below values predicted by the calculations, with the exception of K₂O. HF produces the worst prediction in all cases overestimating the width. Generally, PBE provides the closest description for the valence bandwidth, however LDA is marginally better for the second row oxides.

4. Conclusion

A comprehensive set of data has been compiled to assess the performance of *ab initio* calculations for ionic solids. We have found that no one theory is able to reproduce the electronic structure for these solids. Attempts to assess the basis set effects on the predicted values show that addition of polarised functions to either ion, or additional valence sp shells have minimal effect [7]. Multiple scattering effects have been investigated via Monte Carlo simulations and but do not account for the differences observed [13]. Progress has also been made in modelling the target as a thin layer using slab calculations, however, it has been found that the calculated results become closer to experimental results as the slab thickness increases towards the bulk. Plane wave calculations carried out using a linear augmented plane wave code, WIEN97 can be compared with the LCAO calculations presented here. This comparison suggests improvements in the Hamiltonian, rather than the basis sets, are required to bring theoretical models into better agreement with our experimental results.

Acknowledgments

This work was supported by the Australian Research Council, Flinders University and the University of Technology, Sydney. EA Mikajlo and KL Nixon were supported by SENRAC and Ferry Scholarships respectively.

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