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# The electronic structure of Be and BeO: benchmark EMS measurements and LCAO calculations

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**Abstract**

The electronic band structures of Be and BeO have been measured by transmission electron momentum spectroscopy (EMS). The low atomic number of beryllium and the use of ultrathin solid films in these experiments reduce the probability of electron multiple scattering within the sample, resulting in very clean “benchmark” measurements for the EMS technique. Experimental data are compared to tight-binding (LCAO) electronic structure calculations using Hartree-Fock (HF), and local density (LDA-VWN), gradient corrected (PBE) and hybrid (PBE0) density functional theory. Overall, DFT calculations reproduce the EMS data for metallic Be reasonably well. PBE predictions for the valence bandwidth of Be are in excellent agreement with EMS data, provided the calculations employ a large basis set augmented with diffuse functions. For BeO, PBE calculations using a moderately-sized basis set are in reasonable agreement with experiment, slightly underestimating the valence bandgap and overestimating the O(2s) and O(2p) bandwidths. The calculations also underestimate the EMS intensity of the O(2p) band around the  $\Gamma$ -point. Simulation of the effects of multiple scattering in the calculated oxide bandstructures do not explain these systematic differences.

*Keywords:* M. Metals; O. Oxides; E. Electronic band structure; S. Spectroscopy

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## Introduction

In the same way that electron momentum spectroscopy (EMS) has previously been used to probe the electronic structure of atoms and molecules in the gas phase [1], at Flinders we use the technique to provide measurements of the electronic band structure of the condensed phase [2]. EMS techniques have been refined to the point that it is now possible to map electron momentum distributions with a resolution approaching ‘chemical accuracies’ ( $< 0.2$  eV), allowing a quantitative comparison between measurements and theoretical calculations.

Transmission EMS on solid samples is generally difficult, since measurements are subject to multiple scattering of the electrons within the sample [3, 4]. However, the signal-to-noise ratio is vastly improved when the solid samples are thin ( $\sim 100$  Å), or when they are composed of light elements. In this sense, beryllium and beryllium oxide provide ideal standards with which to test the limits of EMS on solid samples, and the two systems are complementary examples of metallic and insulating solids. Beryllium has a low atomic number ( $Z = 4$ ), and ultrathin films of Be or BeO are readily grown on carbon substrates using standard deposition techniques. The consequent reduction in multiple scattering yields a relatively clean signal in which plasmon excitation and small-angle elastic scattering effects are readily distinguishable from ‘true’ sampling of the bulk electronic band structure.

The low atomic number of beryllium also facilitates theoretical studies of these systems. Beryllium has been the subject of solid state calculations for nearly sixty years, yet still presents a unique challenge to modeling efforts. Although solid Be is nominally metallic, the inter-crystalline bonding has directional ‘covalent’ properties and the solid displays a number of departures from free-electron-like metallic

behaviour [5]. Also, correlation effects between the two electrons in outer valence shell of Be must be taken into account in any realistic model [6, 7]. Similarly, the oxide is often characterised as ionic, yet there are several calculations that predict interstitial charge and directional bonding [8, 9].

Calculations for Be and BeO have traditionally been compared with optical, x-ray and photoemission measurements [10-16]. Generally, these techniques map certain aspects of the band structure such as special-point energies and densities of states, or require considerable theoretical input for their interpretation. The band dispersions for Be have previously been mapped by angle resolved photoemission (ARPES) [17], however a full interpretation of the peak intensities observed in these measurements is complicated by the electron and photon interactions involved. To our knowledge ARPES measurements for BeO have not previously been reported.

The emphasis of the present work is to present our EMS measurements of the valence band structures of Be and BeO to demonstrate the utility of the technique and provide a set of benchmark experimental data. EMS can measure directly the band dispersions and intensities, and provides information complementary to photoemission and other established techniques. In addition, the metal and its oxide are complimentary types of solids representing more itinerant or more localised electronic systems respectively. Whether a particular theoretical method is ‘universal’ can then be tested to a reasonable degree by application to both these solids. We compare our measurements to tight binding (LCAO) calculations using the CRYSTAL98 suite of programs [18]. The calculations have been spherically averaged to account for the structure of the target, and multiple scattering effects included for both systems using a Monte Carlo procedure. For both Be and BeO, we find reasonable agreement between EMS measurements and calculations using

density functional methods (DFT) coupled with moderately-sized basis sets. There is, however, a systematic overestimation in the predicted bandwidths for BeO even after the inclusion of spherical averaging. For metallic beryllium, we perform calculations with two different sizes of basis sets, and find that bandstructures predicted by the larger basis are in better agreement with experimental results. The predicted band intensities for Be show significant deviations from the experimental data which can be explained in terms of many-body effects. For BeO we observe considerable intensity in the O ( $2p$ ) band around the  $\Gamma$ -point whereas the predicted intensity is small, a difference which is not readily explained by multiple scattering.

In the following sections, we first give specifics of the EMS measurement, the sample preparation and the theoretical calculations in this study. We next present the data analysis, including a quantitative comparison of our experimental measurements to the LCAO calculations, and discuss in more detail some of the conclusions we draw from these results.

## 1. Experimental Methods

A number of detailed accounts of EMS can be found in the literature, here we give an overview of the salient points of the experiment [1, 3]. EMS is an electron impact technique, which utilises ionisation of the target to probe electronic structure. In the Flinders spectrometer [19], an incident electron beam of nominally 20.8 keV energy impacts on an ultrathin, self-supporting solid target. Two energy and angle selective electron analysers are positioned on the opposite side of this target to the incident beam. One analyser is set to detect electrons leaving the impact at nominally 19.6 keV and  $13.6^\circ$  relative to the incident beam, and the other at nominally 1.2 keV and

76°. A schematic diagram of the scattering geometry is shown in Figure 1(a). Electrons detected in the analysers can originate from a variety of scattering events - in EMS we are interested in only a small fraction of these: single ionisation of the target. To discriminate these ionisation events from unwanted events, a time coincidence detection method is used, where the time difference between pairs of electrons detected at the two analysers is measured. Two electrons which originate from the same ionisation event will arrive at the two analysers at essentially the same time, i.e. in coincidence. Pairs of electrons from other events give a random distribution of time differences.

The scattering geometry of the spectrometer is chosen so that the ionisation event can be described as a direct knockout of the target electron by the incident electron – the so-called (e,2e) process [20] – with momentum transferred only to the target electron. The ion core is a spectator in the process. Hence we know the energies and momenta of the incident and two outgoing electrons and can therefore determine the energy and momentum of the target electron the instant before it was ejected from the target. The analysers detect electrons over a small window of energies and range of angles. By measuring the number of coincidence events as a function of the energies and angles of the two electrons we build up a probability map of the bound target electrons having a particular binding energy and momentum. In other words EMS provides a direct measurement of the band dispersion *and* density of occupied states for the target solid.

Since this is a transmission measurement, the target has to be extremely thin in order to minimise multiple scattering of the incident or outgoing electrons. In practice targets must be self-supporting and no thicker than about 10 nm. Targets are easily prepared by standard evaporation techniques; Be is evaporated onto an amorphous

carbon film nominally 3 nm thick to form an overlayer of approximately the same thickness. Evaporation is carried out in situ under UHV conditions, the base pressure of the evaporation chamber is about  $10^{-10}$  Torr rising to typically  $10^{-8}$  Torr during evaporation. The oxide samples were prepared by heating Be targets to about 600 °C in an oxygen atmosphere of  $3 \times 10^{-7}$  Torr for about 20 minutes. Overlayer thickness was monitored using a quartz crystal microbalance. The relatively small escape depth of the slower 1.2 keV ejected electron means that the coincidence signal comes predominantly from about the outermost 2 nm of the target. This is sufficiently depth sensitive that the am-C substrate does not contribute to the measured band structure yet not so surface sensitive that reaction of the surface with residual gases present in the vacuum during the measurement becomes a problem. Data are collected over a 2 to 3 day period in order to build up sufficient statistics.

The quality of the prepared targets can be characterised using Auger electron spectroscopy as shown in figures 2(a) and (b). In figure 2(a) the Be KVV line is clearly present together with a small peak at 270 eV attributable to the carbon KLL line. In 2(b) the Auger spectrum shows a clear shift of the Be line together with the O KVV line at 512 eV indicating formation of the oxide.

## 2. Computational Methods

### 3.1 *Ab Initio* LCAO Calculations

Theoretical band structures for Be and BeO were derived from self-consistent Hartree-Fock (HF) or density-functional tight-binding calculations using CRYSTAL98 [18]. DFT calculations included a local density approximation (LDA), a generalised gradient approximation (GGA), and a hybrid method incorporating HF

exchange. LDA results were obtained with Dirac-Slater exchange [21] and Vosko-Wilk-Nusair correlation [22], and GGA results were obtained with Perdew-Burke-Ernzerhof (PBE) exchange and correlation [23]. The hybrid method used was PBE0, developed by Adamo and Barone [24].

Calculations were performed with all electron basis sets specifically optimised for Be and BeO. For metallic beryllium, two basis sets were used: a small 5-111G basis developed by Dovesi and coworkers [6], and an extended 5-1111-(3*p*)-(2*d*) basis – ‘vtz1’ – developed by Grüneich and Heß [25]. The vtz1 basis contains diffuse *s* functions specifically optimised to yield energies with 1mH of the HF limit, yet avoid numerical errors due to linear dependencies in periodic calculations. For BeO, the valence electronic structure is comprised mainly of O(2*s*) and O(2*p*) orbitals, so only moderately-sized basis sets were used in the calculations, namely 5-11G for Be<sup>2+</sup> and 8-411-(1*d*)G for O<sup>2-</sup> developed by Lichanot and coworkers [9].

To assess the performance of the two Be basis sets, minimum-energy structures and cohesive energies were calculated for each basis using HF and DFT methods. Results are listed in Table 1. Calculated values for the HF results are slightly different than those reported by Dovesi *et al.* [6], and Grüneich and Heß [25], with the variance (< 1%) likely due to different SCF convergence properties and tolerances used in the respective calculations. The vtz1 basis gave better predictions for the experimental lattice parameters [26] than 5-111G for HF and DFT, albeit with a nearly ten-fold increase in computational effort. However, cohesive energies closer to the experimental value of 76.6 kcal/mol [27] were obtained with the smaller basis using PBE and PBE0 density functional methods.

A comparison of the calculated LDA band dispersions and electron momentum densities for metallic Be using the 5-111G and vtz1 basis sets are shown in Figure 3.

Here and elsewhere in this paper, electronic structures have been calculated at the experimental lattice parameters. The experimental band dispersion derived from the EMS data also shown and will be discussed in the section 4. EMS dispersion is a spherical average over all crystal directions, experimental data is the same in each panel of figure 3. It is clear in this figure that the use of the more computationally expensive vtz1 basis set yields a slight improvement in the predicted electronic structure, with the 5-111G basis set giving a band dispersion 5 %larger than the vtz1 basis.

### *3.2 Spherical Averaging and Multiple Scattering*

The experimental targets prepared by the above methods are expected to have a polycrystalline structure, therefore the measured band structures represent a spherical average over all crystal directions. In order to directly compare theoretical models to EMS measurements, a spherical averaging of the bandstructure calculation was performed via Monte Carlo sampling of the irreducible wedge of the Brillouin zone (IBZ) of Be or BeO. The Monte Carlo procedure produces 25 equally spaced crystal directions within the IBZ, and the band dispersion and electron momentum density (EMD) is then calculated using CRYSTAL98 along these 25 directions. The EMD is folded into the corresponding dispersion curve and the 25 results summed together. The spherical averages are then convoluted with gaussian functions representing the experimental resolutions in momentum and energy. The resulting energy and momentum resolved density can then be compared directly to the output of the EMS spectrometer.

Despite the thin targets and relatively low atomic number of the targets, the experimental data are still influenced by multiple scattering. The incident or outgoing



electrons can undergo, in addition to the ionisation event, other elastic or inelastic scattering processes, giving rise to a background in the EMS data. In order to account for this in the calculated data we have developed a Monte Carlo procedure to simulate multiple scattering that can be applied to both the (monatomic) metallic and (diatomic) ionic samples. The input to the code is the spherically averaged LCAO calculation. The Monte Carlo procedure is used to determine whether and how many multiple scattering events the electrons undergo and modifies the LCAO energy-momentum density accordingly. Probabilities are assigned to the various processes - namely bulk and surface plasmon excitation, valence electron excitation, and elastic scattering - based upon their mean-free path as calculated from input parameters.

The code used in the present work is based upon that of Vos and Bottema [28] but contains an improved description of the scattering processes and a simple model to simulate systems containing two atom types. For BeO, a calculated Rutherford scattering cross-section from the  $O^{2-}$  and  $Be^{2+}$  ions has been used to simulate the elastic contribution to multiple scattering. A cut-off of 0.5 Å has been applied to these cross-sections since they tend to infinity as the scattering angle approaches zero. For metallic Be, the Born cross-section for the neutral atom is used, and no cut-off is required as the cross-section is finite over all scattering angles.

The left-hand panels in figures 4(a) and (b) show the spherically averaged LDA calculations with the Monte Carlo simulation for Be (5-111G basis) and BeO. In the case of the Be calculation, the Monte Carlo simulation includes an additional convolution to account for electron-hole lifetime effects which are known to be important in the metal [17]. The effect of spherical averaging is close to a simple summation over the five directions shown in figure 3. Some of the detail within the band structure will tend to be smeared out in the process, such as the band gaps or

small departures from free-electron behaviour at the Fermi surface. Multiple scattering produces a background in the data which smears intensity along the energy axis for inelastic processes, and along the momentum axis for elastic scattering. Small angle elastic scattering is the dominant multiple scattering effect in the oxide, resulting from a rapid increase in the Rutherford cross-section at small angles and hence small mean-free path for the process. Conversely, in the metal it is inelastic processes that make a significant contribution producing an overall background and ‘ghost’ bands below the O(2s) valence band due to valence electron and plasmon excitations.

### 3. Results and Discussion

The right hand panels of figures 4(a) and (b) show the measured energy and momentum resolved densities for Be and BeO respectively. The binding energies in these plots are relative to the vacuum level of the spectrometer; the same reference point will be used throughout this paper. Calculated binding energies in figure 4 have been shifted to match the  $\Gamma$ -point energy of the O(2s) band from the experiment. This accounts for the fact that the calculation is performed relative to the Fermi level.

Because EMS measures real electron momentum rather than crystal momentum, our band structures are in the extended zone scheme and are labeled in atomic units (a.u.) of momentum rather than the more familiar symmetry points of the Brillouin zone. The overall energy and momentum resolution of our spectrometer is 1 eV and 0.1 atomic units (a.u.) respectively.

The predicted band structures and background simulations reproduce the general features of the measurement in figures 4(a) and (b). For Be the result is a simple parabola indicative of a metallic (free-electron-like) system which stands out clearly

from the multiple scattering background. A faint second parabola can be seen at an additional energy loss of about 19 eV, this is due to excitation of a single bulk plasmon by the incoming or outgoing electrons. This feature is reproduced by the Monte Carlo simulation.

The BeO bandstructure is characterised by two valence bands derived from the O(2p) and O(2s) orbitals. As expected for an insulating system, both bands are less dispersive than for metallic Be. Once again the EMS signal is relatively clean and the band structure stands out clearly from the multiple scattering background. Small angle elastic scattering is the dominant process which tends to smear intensity within the band structure along the momentum axis. A faint parabola is also visible in the experimental data, we believe this is due to the carbon substrate onto which the Be is evaporated.

To provide a quantitative analysis of the data, we take vertical slices through the data in figure 4 spanning narrow momentum ranges (typically 0.1 or 0.05 a.u.). The result is a series of binding energy profiles at different momentum values, and the peaks in these spectra can then be fitted to extract the band dispersions, bandwidths and intervalence bandgaps. A least squares fit using a combination of a 3<sup>rd</sup> order polynomial for the background and one or two Gaussians for each binding energy peak was used for both the Be and BeO experimental data. Two Gaussians were required to account for small shoulders present on the peaks, and in all cases the fit qualities were extremely high. Fitting the data in this manner allows us to determine the peak positions to greater precision than the independent error in individual data points, or resolution of the experiment. From the least squares fitting procedure we estimate that the overall precision of peak positions is  $\pm 0.15$  eV. The spherically

averaged calculations have also be fitted in a similar manner. We present and discuss the results of this analysis for Be and BeO in the following two sections.

#### 4.1 Be

Experimental and calculated binding energy profiles over 0.1 a.u. momentum intervals are shown in Figure 5. A smooth background has been subtracted from the EMS and calculated data using a 3<sup>rd</sup> order polynomial. The calculations are spherically averaged LDA / 5-111G and LDA / vtz1, and include a simulation of multiple scattering and electron-hole lifetimes through the Monte Carlo procedure. Comparing calculated results obtained with the two different basis sets, it is clear that the extended vtz1 yields can also be seen in the calculated dispersion curves of figure 3, and holds true for the HF and DFT Hamiltonians also employed in this study.

There is reasonable overall agreement between the predicted peak positions and intensities compared with the experimental data. Agreement in the peak intensities requires lifetime effects to be included in the calculation. The inverse lifetime is largest at the bottom of the band ( $q = 0.0$  a.u.) and decreases up the parabola. The intensity within the band is broadened according to the magnitude of the inverse lifetime. Hence, the net effect is to distribute intensity along the parabola, with the maximum intensity pushed away from the band minimum toward larger momentum values [17, 29].

To provide a direct comparison among all the theoretical methods we list bandwidths in Table 2. These are obtained by finding the energy difference between the calculated Fermi energy and  $\Gamma$ -point energy in the lowest dispersion curve in figure 3. A useful comparison can now be made by obtaining the experimental bandwidth from our data. To this end, we first extract the experimental band

dispersion from data similar to that in figure 5. The data were binned into a finer (0.05 a.u.) momentum interval and the least squares fitting method described above used to extract peak positions. The result is shown in figure 3. Beyond about 1 a.u. in momentum, the binding energy profiles of figure 5 are relatively small and very broad and it is difficult to extract meaningful peak positions. The experimental points plotted in figure 3 beyond 1 a.u. correspond to the energy of the middle of the peak. For this reason the experimental (spherically averaged) bandwidth in figure 3 appears much smaller than the calculated bandwidths. To obtain the full bandwidth requires knowing the work function of the spectrometer, since our binding energies are measured relative to this point. This can be accomplished by comparing the experimental and theoretical binding energy profiles integrated over a 0.8 to 2 a.u. range. The two profiles have the same shape but are shifted in energy, and by normalising the observed and calculated energies at the  $\Gamma$ -point, this shift provides a reasonable estimate of the spectrometer work function. With this method we obtain a value of  $3.2 \pm 0.2$  eV. Our measured energy at the  $\Gamma$ -point relative to the vacuum level of the spectrometer is  $14.3 \pm 0.2$  eV, hence the energy relative to the Fermi level (or bandwidth) is  $11.1 \pm 0.30$  eV

Comparing the data of Table 2, HF overestimates the bandwidth by nearly a factor of 2 irrespective of the size of the basis set used. The larger vtz1 basis set narrows the bandwidths with respect to the 5-111G basis by less than 1 eV for all methods used. Although this results is in some ways expected, it is also surprising given the popularity of HF for predicting optimum crystal structures, and the noticeable superior performance of the extended vtz1 basis set in this regard. Clearly a basis set optimised at the HF level to reproduce physical crystal structures may not necessarily reproduce electronic structures. With the inclusion of electron correlation, all three

DFT calculations give significantly narrower bandwidths that are more in line with the observation, although technically, DFT should not be used for this type of comparison. The LDA and gradient corrected (PBE) methods give best agreement, with the PBE/vtz1 combination reproducing the experimental value to within experimental error. Inclusion of exact exchange in the PBEO hybrid method gives values which are around 2 eV wider than experiment.

Previous experimental measurements of the bandwidth range from  $10.25 \pm 0.5$  eV from the x-ray emission data of Lukirskii and Brytov [10] to 16.88 eV from the k-emission spectrum of Sagawa [12]. Using the same technique, Skinner [11] reported a value of  $13.8 \pm 1$  eV. More recently, in an ARPES measurement, Jensen *et al* [17] obtain a value of  $11.1 \pm 0.1$  eV.

#### 4.2 BeO

The experimental (points with error bars) and spherically averaged LDA (solid line) binding energy profiles are shown in Figure 6. A smooth background has been subtracted from the experimental data with a 3<sup>rd</sup> order polynomial to aid comparison with the calculation: the Monte Carlo simulation (dotted line) is dominated by elastic scattering events and does not reproduce this background.

The spherically averaged LDA calculation reproduces the measured intensity and dispersion of the lower O ( $2s$ ) band relatively well, but does not perform so well for the upper O ( $2p$ ) band, particularly in regard to the intensity distribution. The calculation predicts very little intensity at the  $\Gamma$ -point, whereas we observe considerable intensity. Small angle elastic scattering which smears intensity along the momentum axis will contribute to intensity at the  $\Gamma$ -point, however our simulation of this process using the Monte Carlo procedure does not produce sufficient intensity to

explain the observation. In addition, the shape of the measured and predicted binding energy profiles are quite different. At higher momentum values, the Monte Carlo simulation reproduces the observed profiles well, albeit with much smaller intensity. The intensity ratio between the upper and lower valence bands across the entire momentum range also appears quite different in the experiment compared with the calculation, and again cannot be remedied by including multiple scattering effects in the calculation.

Although it is clear that multiple scattering, particularly elastic scattering, does redistribute intensity in the bands, it is not sufficient to explain the large discrepancy between experiment and theory at small momentum values. It also seems unlikely that the finite momentum resolution of the spectrometer is responsible for this difference, as this has, to some degree, been built into the binding energy profiles through the momentum integration. The anomalous intensity may indicate a contribution of cation states to the predominantly oxygen valence band or that the ionization process itself has some momentum dependence to it. The covalent character of BeO is well known and experimental and theoretical studies point to the importance of including metal ion p-states at the top of the valence band. It seems unlikely that the scattering cross-section is the origin of these differences, as this is believed to be well understood from experiments on atomic and molecular targets. Nevertheless, we find that LCAO calculations predict other aspects of the EMS electronic structures, such as bandgaps and bandwidths reasonably well.

Oxygen intervalence bandgaps at the  $\Gamma$ -point have been obtained in previous x-ray and photoemission measurements of the density of states (DOS). Fomichev [14] reports a value of 21.3 eV, and Lukirskii and Brytov [10], 19.5 eV. Photoemission measurements of Hamrin *et al* [15] give a similar value of 20 eV. Our experimental

result of  $19 \pm 0.2$  eV (listed in Table 3) is consistent with these values. We obtain the experimental value from a least squares fit to the EMS binding energy profiles similar to those shown in Figure 6, but with a 0.05 a.u momentum integration. Although it is a spherical average, this value is comparable to previous values due to degeneracy at the  $\Gamma$ -point.

The DOS bandgaps can be compared directly with ones derived from our calculated dispersion curves similar to Figure 3. Values are given by the first number in each column of Table 3. Hartree-Fock overestimates the bandgap compared with the x-ray and photoemission measurements. The DFT methods give much better agreement, with LDA and PBE underestimating and PBEO giving perhaps the closest agreement. The plane-wave pseudopotential calculation of Chang *et al* [30] predicts a value of 19 eV.

Values from our spherically averaged calculation obtained by fitting the predicted binding energy profiles are also given in Table 3 in brackets. Comparing these values with our experiment, PBE gives the closest prediction. Spherical averaging reduces the predicted bandgap by only about 1 %. It is therefore reasonable to compare our experimental value directly with previous DOS values. This slight change in bandgap arises because there are two separate O  $2p$  bands at the  $\Gamma$ -point: most of the intensity lies in the upper of these bands but the small amount present in the other shifts the spherical average to a lower value.

The above x-ray emission and photoemission measurements give O ( $2p$ ) bandwidths that range from 8.8 [10] to 10.3 eV [14]; our experimental value, on the other hand is  $4.7 \pm 0.2$  eV. Care has to be taken comparing these values because of the effects of spherical averaging, which becomes clear when comparing the calculated bandwidths in Table 3. Spherical averaging reduces the O ( $2p$ ) bandwidth



by about 17 % due to the bands being non-degenerate along different directions at the band minimum. However, the experimental bandwidth is still narrower than the spherically averaged calculations, with HF overestimating by about 40 %, and PBE giving the smallest overestimate at 10 %.

Comparing our calculated bandwidths, derived directly from dispersion curves for BeO, with previously published x-ray and photoemission measurements, the HF calculation underestimates the O ( $2p$ ) bandwidth from the experiments. Including electron correlation effects with the DFT methods produces even narrower bandwidths. This is in contrast to metallic Be where bandwidths are generally overestimated by HF and in reasonable agreement with DFT calculations. Two previous DFT calculations [16, 30] both give a bandwidth of 6 eV. A later x-ray emission measurement of the DOS [16] gives a value of 6.8 eV for the bandwidth, which is more consistent with our calculation and considerably narrower than the previous x-ray and photoemission measurements. The difficulty of comparing photoemission DOS measurements with calculations has been pointed out previously [31], where it was suggested that bandwidths extracted from the photoemission DOS may be broadened by instrumental and thermal effects.

From our calculations, it is obvious that spherically averaging reduces the O ( $2s$ ) bandwidth, in this case by about 10 %. Once again our measured value falls below all the calculations with PBE giving a value just outside the experimental error. Previous experimental measurements do not assign a width to the O ( $2s$ ) band.

#### **4. Conclusion**

In this paper we have presented electron momentum spectroscopy of Be and BeO. EMS is a technique that provides a direct and complete mapping of band structures.

The Be and BeO results are relatively free of the effects of multiple scattering and so can provide a benchmark set of data for the technique and a quantitative comparison with theoretical models. We have also presented LCAO electronic structure calculations within the HF and DFT formalisms. Spherical averaging over all crystal directions (to account for the polycrystalline structure of the target) and multiple scattering effects have been included in our modeling efforts in order to address differences between theory and observation.

The Hartree-Fock method is very popular and has proved quite successful for modeling crystal structures. However, we find strong disagreement between EMS measurements and HF predictions of electronic structure. For Be metal in particular, HF overestimates the bandwidth by nearly a factor of two. Clearly, inclusion of electron correlation is critical in modeling the electronic structures of both the metallic and ionic species. The use of an extended basis set for Be, for its high computational overhead, does not significantly improve electronic structures at the HF level, although its predicted lattice constants are in excellent agreement with experiment.

All three levels of DFT calculation reproduce the EMS results more closely. In the case of the intervalence bandgap in BeO, both LDA and gradient corrected DFT underestimate the experimental value, although gradient corrections (PBE) give larger values. Inclusion of exact exchange (PBEO) increases the bandgap further to the point of overestimating the experimental value. The intervalence bandgap is relatively unaffected by spherical averaging since most of the intensity lies in degenerate bands along different directions at the  $\Gamma$ -point. Therefore our EMS bandgaps can be compared directly with photoemission or x-ray measurements and other calculations. Our results are consistent with previously published values.

Even accounting for the effects of spherical averaging in our data, earlier x-ray and photoemission O 2p bandwidths are considerably wider than either our calculated or experimental values. Contrary to previous measurements, we find that all three of our DFT calculations slightly overestimate the widths of the oxygen valence bands in BeO. For both the 2*p* and 2*s* bands, PBE gives the narrowest width followed by LDA then PBEO. Previous calculations agree with our predictions and the more recent x-ray emission measurement gives a narrower 2p bandwidth that better agrees with the EMS result.

The PBE calculation gives excellent agreement for the bandwidth in Be provided the extended basis set is employed. With the 5-111G basis, all the DFT methods overestimate the bandwidth, LDA being narrowest and PBEO considerably broader. For the extended basis, LDA underestimates and PBEO overestimates the bandwidth.

Overall, the PBE functional within a DFT framework reproduces the measured band energies most accurately, although it must be remembered that strictly speaking DFT only provides the total ground state energy and density and not the quasi-particle energies.

The experimental band intensities, of both Be and BeO are significantly different to model predictions of any level. For the metal, the discrepancies arise from many-body interactions in the form of electron-hole lifetimes. However, the differences in the oxide are not readily explained. Our Monte Carlo simulations indicate that multiple scattering effects are not the primary cause of anomalous intensity. One explanation could be the inability of the model calculations to adequately describe covalent effects in the bonding.

The observed discrepancies between theory and experiment, particularly the difference in O (2p) band intensity and bandwidth for the oxide, warrant further investigation. The thickness of the target used in these measurements may be responsible for these differences. Our future efforts will concentrate on understanding the character of the targets used in the experiment and incorporating this into the modeling, in particular, calculating band structures for slabs rather than bulk since the targets are relatively thin.

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**FIGURE CAPTIONS**

**Figure 1.** (a) Schematic of the spectrometer scattering geometry, shaded areas represent angular acceptance of analysers. (b) Target orientation with respect to incident and outgoing electrons, shaded region represents portion of target contributing to (e,2e) signal.

**Figure 2.** Differential Auger spectra for (a) the metallic Be target and (b) the BeO target.

**Figure 3.** DFT band dispersions and electron momentum densities for Be calculated with the LDA. Experimental (spherically averaged) band dispersion derived from EMS data also shown. Binding energies for the two calculations are relative to the Fermi energy, experimental binding energies are normalised to the 5-111G basis set calculation at the band minimum. Momenta are given in atomic units (a.u.).

**Figure 4.** Energy-momentum resolved densities. The calculation is the spherically averaged DFT LDA with a Monte Carlo simulation of multiple scattering and lifetime effects for Be. Calculated binding energy has been normalised to the experiment at zero momentum. Intensity is on a linear gray scale.

**Figure 5.** Binding energy profiles for Be extracted from the measured and calculated energy-momentum resolved density. Calculations are spherically averaged LDA with the Monte Carlo simulation. A smooth background has been subtracted from all data sets. Calculated binding energy and intensity of the valence band has been normalised to the experiment at 0.0 a.u. momentum.

**Figure 6.** Binding energy profiles for BeO extracted from the EMS measurement and calculated energy-momentum resolved density. Calculations are spherically averaged LDA, with and without the Monte Carlo simulation of multiple scattering. A smooth background has been subtracted from the experimental data. Calculated binding energy and intensity of the 2s band has been normalised to the experiment at zero momentum. The calculated O(2p) peak at 0 and 0.1 a.u. momentum with no Monte Carlo simulation has been scaled upwards by a factor of 10.

**Table 1.**

Calculated and experimental lattice constants and binding energies. The percent difference between calculated and experimental values are given in parentheses.

Basis and method	a (Å)	c (Å)	$E_{\min}$ (au)	$E_b$ (kcal/mol/atom)
HF/5-111G	2.2312 (-2.39)	3.4878 (-2.69)	-29.2500	45.2
LDA/5-111G	2.2016 (-3.68)	3.4908 (-2.61)	-29.1564	94.8
PBE/5-111G	2.2080 (-3.40)	3.4846 (-2.78)	-29.4763	80.9
PBE0/5-111G	2.1961 (-3.92)	3.4694 (-3.21)	-29.4879	79.7
HF/vtz1	2.3141 (+1.24)	3.5959 (+0.32)	-29.3054	56.5
LDA/vtz1	2.2268 (-2.58)	3.5064 (-2.17)	-29.2032	103
PBE/vtz1	2.2610 (-1.08)	3.5622 (-0.62)	-29.5319	91.6
PBE0/vtz1	2.2583 (-1.20)	3.5523 (-0.89)	-29.5419	90.4
Experiment	$2.2858 \pm 2^a$	$3.5843 \pm 2^a$	--	$76.6^b$

<sup>a</sup>ref [26]

<sup>b</sup>ref [27]



**Table 2**

Experimental and calculated Be conduction band widths (eV). Theoretical predictions based upon experimental lattice constants.

Method/basis	Bandwidth (eV)
HF/5-111G	19.52
LDA/5-111G	11.55
PBE/5-111G	11.7
PBE0/5-111G	13.65
HF/vtz1	19.24
LDA/vtz1	10.97
PBE/vtz1	11.13
PBE0/vtz1	13.24
Experiment	$11.1 \pm 0.3$

**Table 3**

Measured and predicted bandwidths for BeO in eV. The first number in each column is the calculated from the dispersion curve, numbers in brackets are from the spherically averaged calculations.

<b>Method</b>	<b><math>\Gamma_1 \rightarrow \Gamma_{1,6}</math></b>	<b><math>\Delta E(\text{O } 2p)</math></b>	<b><math>\Delta E(\text{O } 2s)</math></b>
HF (sph av)	25.22 (24.93)	8.05 (6.77)	2.84 (2.56)
LDA (sph av)	18.47 (18.29)	6.43 (5.39)	2.39 (2.19)
PBE (sph av)	18.73 (18.50)	6.36 (5.30)	2.32 (2.09)
PBE0 (sph av)	20.44 (20.22)	6.88 (5.75)	2.47 (2.27)
Expt.	$19 \pm 0.2$	$4.7 \pm 0.2$	$1.7 \pm 0.2$