

Bulk and surface electronic structure of Li_2O

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We have used photoemission and electron-energy-loss spectroscopies to determine the surface and bulk electronic structure of a single-crystal sample of the alkali-metal oxide Li_2O . The predominately O $2p$ valence band exhibits two main features in the photoemission spectrum, whose relative widths are consistent with results of an *ab initio* Hartree-Fock calculation of the bulk electronic structure. However, changes in the intensity of the two features as a function of the exciting photon energy are large and not understood. Energy-loss spectra show the presence of a strong surface exciton in the bulk band gap of Li_2O ; such excitonic surface states do not exist for the alkali halides. Its energy is about 2 eV less than the bulk band gap, similar to the surface excitonic shifts that have been observed in the alkaline-earth oxides. [S0163-1829(96)05927-9]

I. INTRODUCTION

During the last two decades, extensive theoretical and experimental investigations have been conducted on the alkali-metal oxide Li_2O . The interest in this material is twofold. On the fundamental side, Li_2O is one of the simplest ionic oxides, thus serving as a starting point for, and complementing the study of, other ionic oxides. On the technological side, because of its high Li atomic density and high melting temperature, Li_2O has been considered as a potential candidate for the blanket breeding material in future thermal nuclear reactors. Both theoretical and experimental investigations aimed at understanding the conduction mechanism,¹ the defect energetics and mobility,¹⁻⁴ the phonon dispersion relation,⁵ and the elastic properties⁵⁻⁷ of the oxide have been carried out. In addition, significant effort has been devoted to studies of its thermodynamic properties, its stability under various conditions such as radiation, and the diffusion of impurity atoms inside the material,⁸ as these directly relate to its technological applications.

In first-principles calculations of various properties of Li_2O such as defect energetics, surface stability, and relaxation, the first step is often the calculation of the electronic structure. The study of the electronic structure of this simple s,p -electron oxide is important since it serves to elucidate the interaction between metal s,p and oxygen p states, a prerequisite for the study of more complex oxides such as transition-metal oxides, in which the more localized d electrons are involved. Although there have been several calculational efforts,^{4,7,9} the only experimental data available on the electronic structure of Li_2O have been optical absorption measurements of the bulk band gap and of radiation-induced band-gap defect states.¹⁰ No photoemission spectra of the density of occupied electronic states, or energy-loss spectra of the joint valence and conduction band density of states, have been reported.

In this paper, we report the results of comprehensive measurements of the bulk and surface electronic structure of Li_2O using x-ray and ultraviolet photoemission (XPS and UPS) and electron-energy-loss (EELS) spectroscopies. We find that the predominantly O $2p$ valence band is comprised of two features, whose relative widths are consistent with results of *ab initio* Hartree-Fock calculations.⁹ An unusually strong dependence of the emission intensities of the two features on exciting photon energy is observed. The total valence-band width of Li_2O is found to be about 5 eV, slightly smaller than that of most other oxides, which may be due to its highly ionic nature and to the large O-O distance in Li_2O . A strong excitonic surface state, having an onset energy of 4.3 eV and a maximum intensity at about 5.7 eV in energy-loss spectra, is found in the bulk band gap. This exciton is similar in energy to those that are present on the surfaces of the much more thoroughly studied alkaline-earth oxides, but are absent on alkali halides.

II. EXPERIMENTAL PROCEDURE

A disk-shaped single-crystal sample of Li_2O 8 mm in diameter and 3 mm thick was mounted on a Ta sample holder using silver-based conductive epoxy. The (111) plane of the antifluorite structure of Li_2O was parallel to the disk surface. This same sample had been used in a previous low-energy ion-scattering spectroscopy study.¹¹ In that study, measurements on ultrahigh-vacuum (UHV) cleaved (111) surfaces indicated that the outermost atomic layer was Li^+ . Atomically clean surfaces of Li_2O were obtained in the present study by scraping the (111) surface *in situ* in the surface analysis system using a diamond file. The base pressure of the UHV system was 2×10^{-10} Torr.

XPS and UPS measurements were performed using a Mg x-ray anode at 1253.6 eV and a He discharge lamp at He I (21.2 eV) and He II (40.8 eV) energies. A Physical Electron-

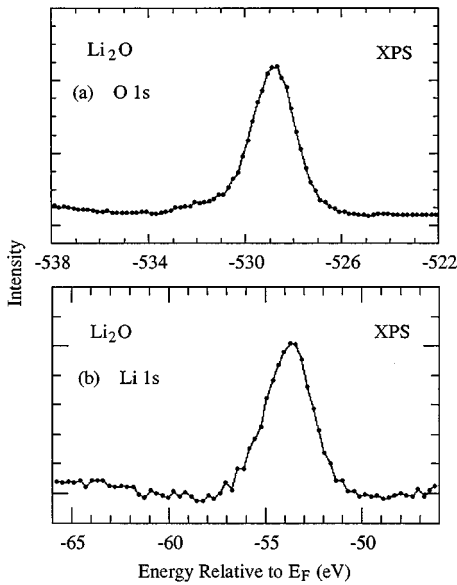


FIG. 1. (a) O $1s$ and (b) Li $1s$ core-level XPS spectra of Li_2O . $h\nu=1253.6$ eV.

ics double-pass cylindrical mirror analyzer (CMA) was used for analyzing the kinetic energies of the electrons in both the photoemission and EELS measurements. The electron gun used in the EELS measurement is the coaxial electron gun in the CMA assembly. The overall energy resolutions for the XPS, UPS, and ELS spectra presented here are 1.0, 0.15, and 0.5 eV, respectively. Sample charging during photoemission measurements was partially compensated for by illuminating the sample with ultraviolet radiation from a Xe arc lamp.

III. RESULTS

Figures 1(a) and 1(b) show the O $1s$ and Li $1s$ core-level XPS spectra of Li_2O , respectively. A distinct feature of both spectra is their symmetric line shapes. This is characteristic of a good insulator, because of the lack of any electron-hole screening process following the creation of the core hole. For metallic or semiconducting materials, core-level spectra often exhibit an asymmetric Doniach-Sunjić line shape,^{12,13} which is skewed toward the higher binding-energy side due to excitonic many-body effects resulting from interactions between the core hole and conduction electron states. Due to the small atomic number of Li, the intensity of the Li $1s$ core-level emission is very small compared to that of the O $1s$.

Figure 2(a) shows the valence-band UPS spectra of Li_2O taken with He I (dots) and He II (line) photons. In addition to the use of the Xe arc lamp discussed above, surface charging was eliminated as completely as possible by reducing the incident He photon flux until no further changes were observed in the spectra. The energy scale used on the abscissa in Fig. 2(a) is referenced to the Fermi level of a gold sample. However, the location of the Fermi level in Li_2O could still not be determined accurately due to the possibility of some residual surface charging. In both spectra the upper edge of the valence band is located at the same position in energy, which is consistent with a stable surface potential. (The He I and He II spectra have been normalized

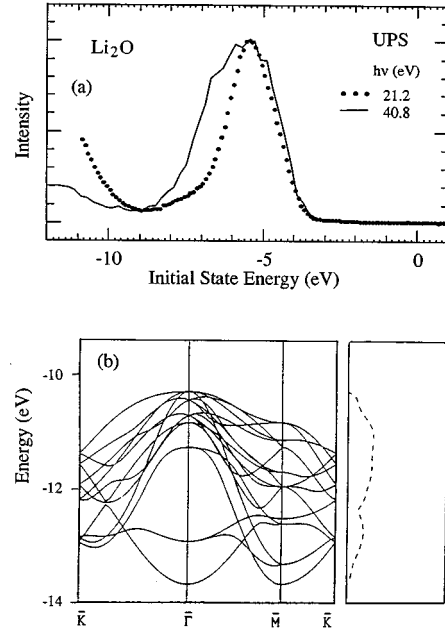


FIG. 2. (a) UPS spectra of Li_2O obtained with He I ($h\nu=21.2$ eV; dots) and He II ($h\nu=40.8$ eV; solid line) photons. See text for a discussion of the initial-state energy scale. (b) *Ab initio* Hartree-Fock calculation of the band dispersion and density of states (right panel) of the valence band of Li_2O . (Adapted from Ref. 9.)

in intensity at the maximum near the upper edge of the band.) The most striking difference between the He I and He II spectra is the much lower emission intensity in the higher binding-energy region of the O $2p$ band (between 6 and 8 eV) in the He I spectrum. This suggests that the valence band basically consists of two structures having different photon energy dependencies. The overall width of the valence band of Li_2O is about 5 eV.

Figure 2(b) presents the results of an *ab initio* Hartree-Fock calculation for the valence band of Li_2O .⁹ The left panel of the figure is the bulk band dispersion projected onto a plane perpendicular to the (111) surface, i.e., the surface Brillouin zone of the (111) plane. The right panel is the density of states.

Figure 3 shows interband EELS spectra of Li_2O taken with primary-electron energies E_p of 55, 105, and 155 eV. The spectra exhibit no loss features for energies less than 4.3 eV; the details of the spectral onset around the band gap are shown in the inset of Fig. 3 for the 55-eV spectrum. In addition to the structure between about 4 and 7 eV, the EELS spectra of Fig. 3 also exhibit two peaks at about 10 and 17 eV.

IV. DISCUSSION

The UPS spectra of the O $2p$ valence band in Li_2O exhibit an interesting photon-energy dependence that has been observed in other non-transition-metal oxides but has not been discussed in the literature. Similar phenomena have been shown previously, without explanation, for the non-transition-metal oxides MgO ,¹⁴ ZnO ,¹⁵ and SnO_2 .¹⁶ The vast majority of UPS studies of the electronic structure of metal oxides have been performed on transition-metal oxides.^{17,18}

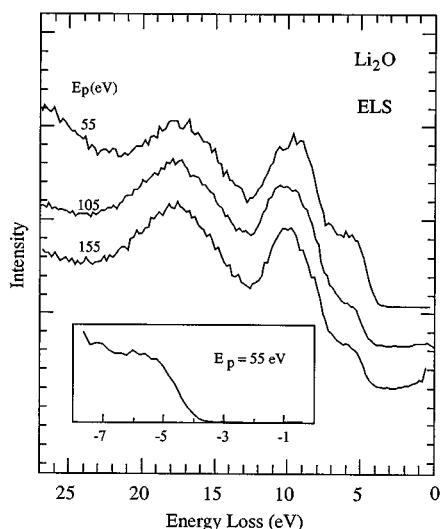


FIG. 3. Electron-energy-loss spectra of Li_2O taken with primary-electron energies of 55, 105, and 155 eV. The inset shows the details of the band-gap loss region for the 55-eV spectrum.

For those compounds, the higher binding-energy region of the O $2p$ valence band contains the largest admixture of cation d -electron wave function that results from cation-anion hybridization; this region is usually referred to as the *bonding* part of the band. The lower binding-energy part of the valence band (i.e., that nearest E_F) is referred to as the *nonbonding* region, since it contains less cation d -electron character. (However, other cation orbital wave functions, such as $4s$ or $4p$ for the $3d$ transition-metal oxides, may hybridize with the nonbonding O $2p$ orbitals.¹⁹) For transition-metal oxides, increasing the photon energy from 21.2 to 40.8 eV results in a *slight* increase in the relative intensity of the bonding valence-band emission, presumably because of the larger cross section for emission from the spatially more localized d orbitals at higher photon energies than from the p orbitals that comprise most of the valence band.

The photon-energy dependence observed here is in the same direction as, but far more dramatic than, that for any transition-metal oxide. The bonding orbital emission almost completely disappears for 21.2-eV photons. This is a surprising observation for two reasons. First, the decrease in intensity at the lower photon energy far exceeds the amount of hybridized cation wave function expected in the O $2p$ band.¹⁸ In addition, it is not at all clear that there should be significant photon-energy dependence to the emission at all, since the hybridized cation orbitals in this case are Li $2s$ and $2p$, whose spatial extent is comparable to that of the O $2p$ orbitals. One might even expect the Li $2s, p$ states to have a *lower* cross section relative to O $2p$ at higher photon energies.^{20,21} We do not currently understand the origin of this behavior.

The width of the valence band in Li_2O observed here—about 5 eV—is comparable to, but slightly narrower than, those for most other metal oxides.¹⁸ MgO, ZnO, and many $3d$ transition-metal oxides have O $2p$ bandwidths of about 6 eV. The valence band in SnO_2 is about 7 eV wide, and Al_2O_3 exhibits a measured bandwidth of about 8 eV. The fact that the valence band in Li_2O is narrower is probably a

result of the somewhat longer O-O distance in Li_2O ; it is 3.27 Å, compared to values of 2.98 Å in MgO, 2.54 and 2.90 Å in SnO_2 , and generally less than 3 Å in transition-metal oxides. The exception to this trend is ZnO, which has an O-O distance of 3.25 Å; it is also the only other oxide whose cations are tetrahedrally coordinated with O ions, as are the Li^+ ions in Li_2O .

The density-of-states calculation shown in the right panel of Fig. 2(b) shows that two structures are predicted in the valence band: one comprising the lower binding-energy (nonbonding) region, and one forming the higher binding-energy (bonding) region. The former has a width in energy about twice that of the latter. This is generally consistent with the observations in the UPS spectra shown in Fig. 2(a) and the discussions in the preceding paragraph. The calculation⁹ did not discuss any differences in orbital character between states in the lower and higher binding-energy regions; thus they provide no insight into the observed strong photon-energy dependence of the two features. The width of the valence band obtained from the calculation is only 3.5 eV. While this is less than the value of 5 eV obtained from the valence-band UPS spectra, it is not surprising, since Hartree-Fock calculations tend to underestimate bandwidths (and overestimate bandgaps).²¹ There may also be some contribution from photohole lifetime broadening in the UPS spectra, as well as from uncertainties in locating the top and the bottom edges of the valence band.

Optical absorption measurements on both single-crystal and sintered polycrystalline Li_2O have shown that the fundamental valence-to-conduction band gap is greater than 6 eV.¹⁰ Because of the very short mean free paths of low-energy electrons in solids (as short as a few atomic planes), EELS spectra are able to see surface valence-to-conduction-band transitions that do not appear in optical absorption. Such transitions are referred to as *surface excitons*, and they have been studied extensively in the alkaline-earth oxides.^{18,22–26} In MgO, the onset of loss features in EELS spectra is at 6 eV, while the bulk band gap is 7.8 eV. The surface origin of the lowest-energy loss feature was clearly demonstrated for MgO by varying the incident-electron energy from a surface-sensitive value of 100 eV up to a value of 2000 eV, which probes predominately the bulk electronic structure.^{23,24} However, such surface excitonic transitions have not been previously reported in the alkali-metal oxides. For the alkali halides, in fact, EELS spectra exhibit excitations identical to the bulk transitions measured by photoemission. Attempts to rationalize the difference between alkali halides and alkaline-earth oxides have included the suggestion that surface excitons only exist if the conduction band lies above the vacuum level for the surface.²² Unfortunately, it has not been possible to accurately determine the vacuum level for these materials due to surface charging.

Although a much narrower range of incident-electron energies was available in the spectra presented here than was used in Refs. 23 and 24, some primary-electron-energy dependence is observed in the lowest binding-energy feature in the EELS spectra. The amplitude of that feature, which has an onset energy of 4.3 eV and a maximum intensity at about 5.7 eV, is largest for $E_p = 55$ eV, decreasing by about one-

third upon increasing E_p to 105 eV; no significant change is seen when further increasing E_p to 155 eV. The relative amplitude and width of the loss features at 10 and 17 eV do not depend on primary-electron energy. This strongly suggests that the loss threshold at 4.3 eV arises from a surface excitation; however, EELS measurements over a much wider incident-electron energy range would be required in order to completely determine that.

The loss feature that has a maximum at about 10 eV in Fig. 3 has its onset at 7–7.5 eV. That is consistent with optical absorption measurements of the bulk band gap in Li₂O.¹⁰ The initial states for the 10- and 17-eV loss features must lie in the O 2*p* valence band; the next higher binding-energy core level—the O 2*s*—lies too far down in energy. The final state for the 10-eV transition is almost certainly the Li 2*s*,*p* band, although calculations of the location of those empty orbitals have not been reported. (The final state for the 17-eV loss feature could be either a Li or an O orbital; not enough is known about excited states in Li₂O to be more specific.) Since neither the 10- nor the 17-eV loss peaks exhibit any primary-electron-energy dependence, they presumably correspond to bulk transitions. The shift in energy below the bulk band gap of the surface exciton seen in Fig. 3 is consistent with values observed for the alkaline-earth oxides.

V. SUMMARY

We have performed measurements of the bulk and surface electronic structure for the ionic oxide Li₂O using XPS, UPS, and EELS spectroscopies on a single-crystal sample. The predominately O 2*p* valence band structure is found to be in generally good agreement with the results of an *ab initio* Hartree-Fock calculation, although there is a strong dependence of the relative intensity of the two primary features in the valence band in UPS with incident photon energy. This dependence has been observed in other non-transition-metal oxides, but its origin is not understood. A strong excitonic surface state is observed on Li₂O by using electron-energy-loss spectroscopy. Such surface excitons are not observed for the alkali halides. However, very similar excitonic states have been observed on alkaline-earth oxide surfaces. It has been speculated that the existence of such states is associated with the position of the conduction-band edge relative to the vacuum level of the material.

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