

Oxygen x-ray emission and absorption spectra as a probe of the electronic structure of strongly correlated oxides

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We present synchrotron-excited oxygen x-ray K -emission spectroscopy (O $K\alpha$ XES) and oxygen x-ray absorption spectroscopy (O $1s$ XAS) spectra of transition-metal (TM) oxides MnO, CoO, and NiO. The comparison of oxygen K -emission and absorption spectra to valence band photoemission and bremsstrahlung isochromat spectra measurements shows that O $1s$ XAS is not strongly influenced by the core hole effect, whereas the TM $2p$ XAS significantly shifts to a lower energy. New and effective methods for determining the band gap and anion-to-cation charge-transfer energies of the oxides from the measured spectra are presented and applied, and the combination of O XAS and XES is shown to agree well with the results of numerical electronic structure methods applied to strongly correlated oxides. For MnO, the charge-transfer energy is found to be 6.6 eV and the band gap is 4.1 eV; for CoO, the values are 6.1 and 2.6 eV and for NiO, the values are 5.4 and 4.0 eV.

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I. INTRODUCTION

Strongly correlated electron systems have attracted a great deal of attention in recent years because they show interesting physical properties, including metal-to-insulator transitions, magnetic phase transitions, and ultrafast switching phenomena, which can be controlled by small changes in externally applied fields. Effective models of the material properties of weakly correlated solids can be developed from first-principles spin density functional theory¹ calculations by using a local density approximation (LDA).² However, the consideration of strongly correlated systems containing d and f electrons is somewhat more complicated. For such materials, LDA is an inadequate approximation if the on-site Coulomb interaction (U) between electrons is relatively strong, i.e., if the magnitude of U approaches or exceeds that of the bandwidth (W).³ The Mott–Hubbard and charge-transfer insulators and heavy fermion metals cannot be well described within this framework. When applied to insulating transition-metal (TM) monoxides, the LDA approximation incorrectly predicts very small (for MnO and NiO) or non-existent (for CoO) band gaps.⁴

The band structure theory of strongly correlated electron systems was significantly improved by the development of the LDA+ U method, a Hartree–Fock-type scheme, which is able to account for a variety of the important properties of transition-metal compounds,⁵ such as the ground states of phases that are magnetically charged or orbitally ordered. The static LDA+ U approach is not sufficient to describe the effects of excitations on the electronic structure, and thus, it is not suitable for describing photoemission spectra. Combining LDA with dynamical mean field theory (DMFT) into a complete LDA+DMFT scheme provides a much more accurate model of such effects.⁶

It is well known that the basic electronic structure, band gaps, and superexchange interactions in TM oxides are mostly determined by a few fundamental quantities, such as on-site Coulomb interactions U , the charge-transfer energy Δ , and the one-electron bandwidth W , and so experimental determination of these properties is essential. Photoemission [x-ray photoemission spectroscopy valence band (XPS VB) and ultraviolet photoemission spectroscopy] and isochromat [bremsstrahlung isochromat spectroscopy (BIS) and inverse photoemission spectroscopy] spectroscopies are commonly combined to provide complete experimental single-particle spectra and to assess the performance of different theoretical models of the electronic structures of strongly correlated systems (see, for instance, Ref. 7); both techniques are, however, extremely surface sensitive. In this paper, we show that the combination of the bulk-sensitive oxygen x-ray emission and absorption spectra of NiO and MnO agrees well with previously published XPS VB and BIS spectra, which is in marked contrast to the metal L -edge spectra, in which the influence of the core hole leads to significant discrepancies in the energies. With this established, we use our measured spectra to determine values for the band gap and anion-to-cation charge-transfer energy of MnO, CoO, and NiO.

II. MATERIALS AND METHODS

The x-ray emission spectroscopy (XES) spectra of MnO, CoO, and NiO were measured at beamline 8.0.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The x-ray absorption spectroscopy (XAS) spectra were measured by using the spherical grating monochromator beamline at the Canadian Light Source at the University of Saskatchewan. The O XAS spectra were measured in the total fluorescence yield (TFY) mode, which provides more

bulk sensitivity than electron yield methods do. The effects of self-absorption on the metal edge TFY spectra were pronounced, but they agreed in energy with the total electron yield spectra that are presented below. The O $K\alpha$ XES was excited near the O $1s$ ionization threshold to suppress the high-energy satellite structure. The estimated experimental energy resolution was approximately 0.5 eV for the XES and 0.1 eV for the XAS measurements. MnO, CoO, and NiO (99.99%) powders obtained from Aldrich were used without further refinement.

The x-ray emission and absorption spectra reflect the local density of occupied and unoccupied electronic states, respectively; the presence of the core hole that is created during the absorption process modifies, to varying degrees, the information acquired through both techniques. The relative effects of the core hole on the measured densities of states (DOS) are governed by the final state rule,^{8,9} meaning that absorption measurements, in which the core hole is a part of the final state, are more strongly affected than emission measurements, in which the final state vacancy is in a valence state. In the case of the transition-metal oxides, the O $1s$ core hole created during the XAS measurements is expected to weakly interact with the TM $3d$ states. These states appear in the O $1s$ XAS spectra as transitions into hybridized O $2p$ /TM $3d$ states and so it is expected that these measurements should provide a relatively unperturbed probe of the TM DOS.

The core hole effect in O $1s$ XAS for NiO is quantitatively studied in Ref. 10 on the basis of LDA+ U calculations. Very strong Ni $3d$ -O $2p$ hybridization is found over the entire energy range of the valence and conduction bands. The calculated spectrum of Ref. 10 reproduces the fine structure of the O $1s$ XAS quite well; as expected, the lowest-energy conduction states are formed by O $2p$ /Ni $3d$ hybridization. The lack of interaction between the core hole and the conduction band states is, importantly, confirmed by the observation that the partial O $2p$ density of states with the core hole *does not differ* from that calculated without the core hole. This observation is unsurprising, given the fact that the $3d$ orbitals are centered on the transition-metal site away from the O $1s$ core hole, and so a strong interaction is not expected.

The estimation of the band gap from the measured O K -edge XES and XAS spectra is achieved through a relatively simple procedure. In order to avoid the uncertainties involved with the fitting of tangent lines to determine the location of, for example, the absorption onset, a method based on the second derivative of the measured spectra is used. The second derivative of the XES and XAS spectra of a sample is plotted on a common energy scale, and the distance between the highest-energy peak of the XES derivative and the lowest-energy peak of the XAS derivative is determined. The suitability of the material being studied must be taken into account when applying this method, as the presence of strong resonant inelastic x-ray scattering (RIXS) effects will have an effect on the location of the absorption edge. We do not anticipate that this will have a significant effect in the results obtained in this study, given the weakness of the RIXS effects that would be observed as a result of excitation into the hybrid O $2p$ /M $3d$ state. These points cor-

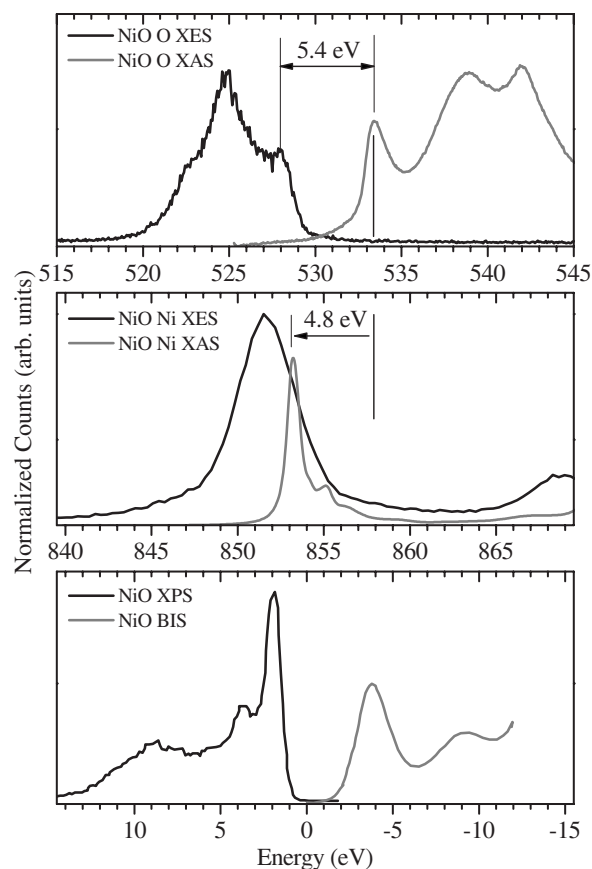


FIG. 1. The comparison of oxygen K - and Ni L -emission and absorption spectra to XPS VB and BIS of NiO.

respond to the onsets of the densities of states on either side of the gap. It will be shown that the application of this procedure to transition-metal oxides yields values that are in close agreement with published values.

The anion-to-cation charge-transfer energy is also graphically estimated from the XAS and XES plots. In a simple one-electron picture, the charge-transfer energy is defined as the energy required to move an electron from the highest lying occupied oxygen $2p$ state to the lowest lying unoccupied metal $3d$ state. The energy level of the ligand state can be directly read from the O XES spectrum, and the lowest-energy feature of the O XAS spectrum is used to approximate the energy of the metal state. The absence of a hole in the ligand valence electronic structure is not expected to have a significant effect on the energy of this state, although this unavoidable inconsistency between our method and the definition of Δ must be noted.

III. RESULTS

In Fig. 1, we compare oxygen and nickel x-ray emission and absorption spectra to the XPS VB¹¹ and BIS¹² spectra of NiO. The relative positions of the x-ray emission and absorption spectra with respect to the XPS VB and BIS spectra (displayed on the binding energy scale) are chosen by taking into account the XPS binding energies of the core levels [$E_{\text{be}}(\text{Ni } 2p_{3/2})=854.1$ eV, $E_{\text{be}}(\text{O } 1s)=529.4$ eV].¹¹ The en-

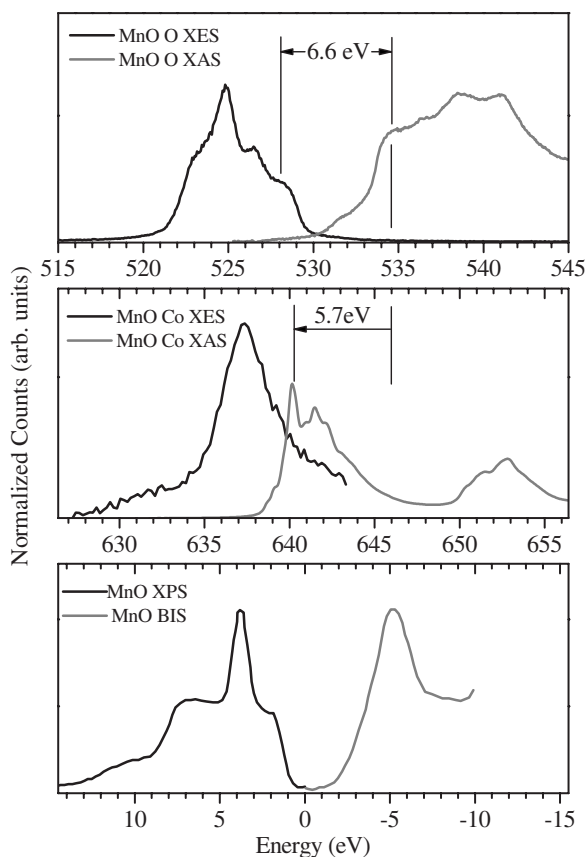


FIG. 2. The comparison of oxygen K - and Mn L -emission and absorption spectra to XPS VB and BIS of MnO.

ergy calibration of the XAS and XES data was performed by comparing the recorded spectra to a subsequently recorded spectrum of a known reference sample. The lowest-energy peak of O $1s$ XAS aligns well with that of the BIS spectrum, whereas the intensity maximum of the Ni $2p$ XAS is shifted to a lower energy by about 4.8 eV, indicating a strong core hole effect in the TM $2p$ x-ray absorption spectra.

Similarly, the comparison of the MnO (Fig. 2) and CoO (Fig. 3) XAS and XES spectra to XPS VB-BIS^{11,13,14} in Fig. 2 yields a similar result, with the effect of the core hole causing shifts of -5.7 eV in the Mn XAS and -5.0 eV in the Co XAS. The correspondence between the O K -edge XAS and XES and the XPS-BIS data demonstrate that bulk-sensitive soft x-ray fluorescence measurements can be used in the study of correlated systems, eliminating the need for difficult surface preparations.

The experimental oxygen K -emission and absorption spectra can be used to estimate the anion-to-cation charge-transfer energy by measuring the energy difference between the lowest O $1s$ XAS peak and the highest O $K\alpha$ XES peak. By using the data presented in Figs. 1–3, the numerical values of Δ are found to be 6.6 eV (MnO), 6.1 eV (CoO), and 5.4 eV (NiO). Previously published values were obtained through indirect means, with Δ appearing as a parameter in the fitting of core level XPS data, and therefore, there have been a wide range of values reported. The results obtained through our method are in general agreement with a representative sample of previous reports: 7.0 for MnO,¹⁵ 6.0 for CoO,¹⁶ and 6.2 for NiO.¹⁶

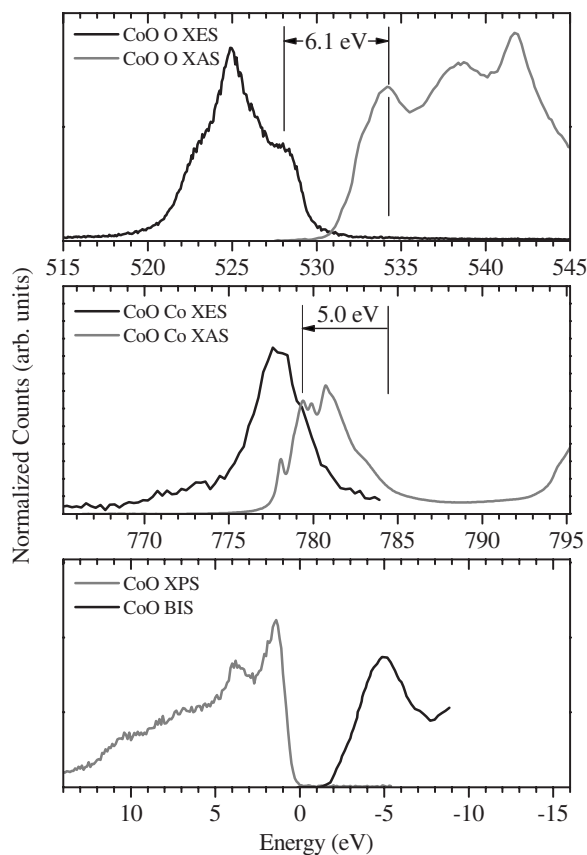


FIG. 3. The comparison of oxygen K - and Co L -emission and absorption spectra to XPS VB and BIS of CoO.

The determination of the band gap, as described in Sec. I, was performed by using the measured XES and TFY absorption spectra. The plots of the second derivatives of the spectra are shown in Fig. 4, with the peaks corresponding to the band gap edges marked. As a rule, the peak that occurs next to the first inflection peak of the rising spectral edge was used for the measurements. The obtained values for the MnO, CoO, and NiO band gaps were 4.1, 2.6, and 4.0 eV, respectively. All of these values agree with previously published values [4.0,¹⁷ 2.5,¹⁸ and 3.9 eV (Ref. 19)] within experimental resolution. This finding is significant, given the notorious difficulties involved in the accurate determinations of band gaps.

As shown above by the comparison to the XPS VB/BIS data, the O K -edge spectra essentially reflect the single-particle spectral function, and so they can be used to directly evaluate the validity of different theoretical approaches to the study of TM oxides. In Fig. 5, we compare our oxygen K -emission and absorption measurements to the O p spectral densities obtained by different theoretical approaches. The LDA+ U ($U=4.6$ eV) calculations performed by Cococcioni and Gironcoli²⁰ make use of a plane-wave pseudopotential model and also rely on an internally consistent method for determining the value of U that is to be applied; the full details of the comparison with the generalized gradient approximation (GGA) calculations (also shown) are included in the original publication. While the GGA²⁰ appears to reproduce the overall shape of the XAS and XES spectra, it un-

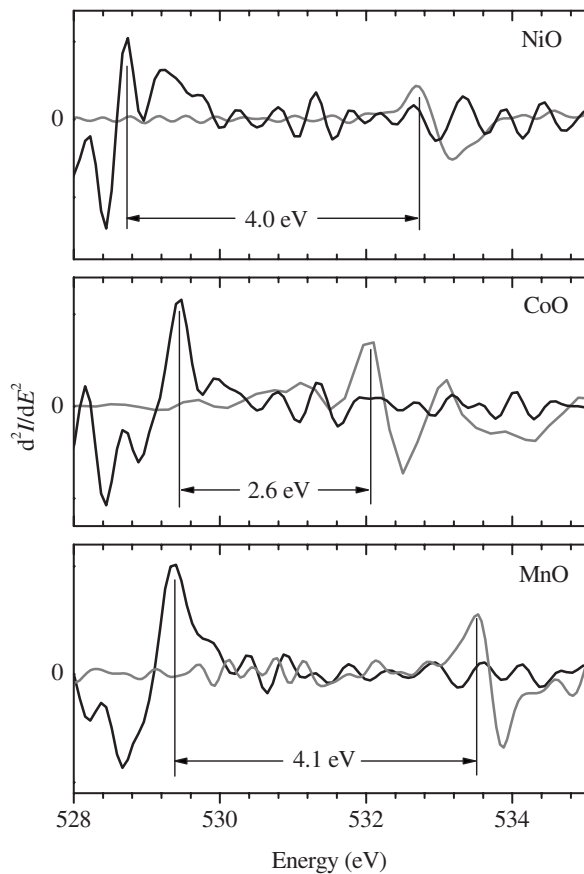


FIG. 4. The estimation of band gap for NiO, CoO, and MnO from oxygen K -emission and absorption spectra.

derestimates the gap. The LDA+ U spectrum of Ref. 20 overestimates the $O p$ spectral weight at the top of the valence band. Finally, we show the $O p$ spectrum of Ref. 21 that is obtained with the LDA+DMFT method at 1160 K by using the same U parameter ($U=8$ eV) as in Ref. 5. One should also point out that both the GGA and the LDA+ U spectra of Ref. 20 fail to describe the incoherent -8 eV peak in the XPS VB spectrum, while the dynamical treatment of the local correlations and p - d hybridization of Ref. 21 provides a very good match with the present x-ray data as well as with XPS VB spectra.

In summary, synchrotron-excited oxygen x-ray emission and absorption spectra of MnO, CoO, and NiO were measured and it is found that the electronic relaxation of the $O 1s$ core hole effect is negligible. It is concluded that these spectra can probe not only $2p$ but also $3d$ states due to a strong $2p$ - $3d$ hybridization. The energy difference between the centers of gravity of the high-energy subband of $O K\alpha$ XES and the first peak of $O 1s$ XAS can be used for the estimation of the charge-transfer parameter Δ . A method for determining a material's band gap from analysis of its XES and XAS spec-

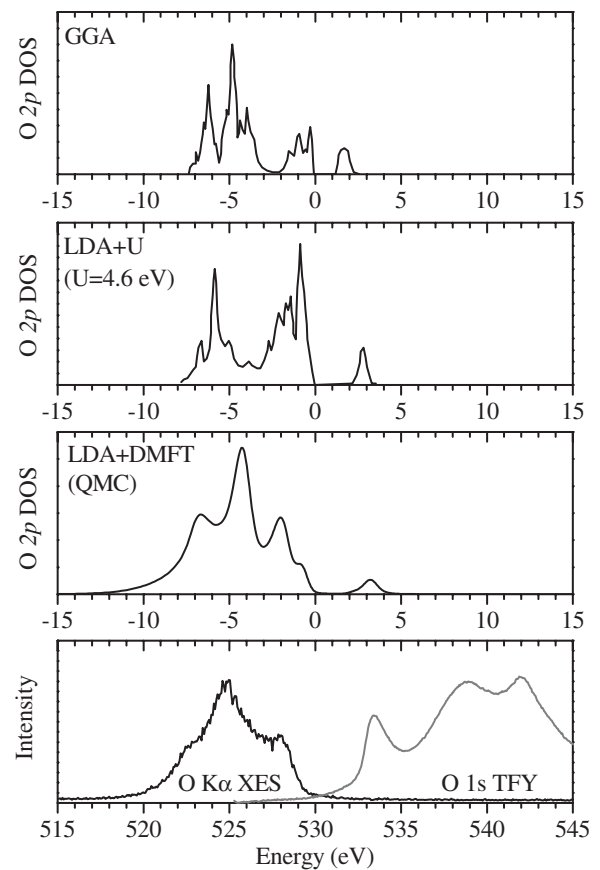


FIG. 5. The comparison of $O 2p$ DOS of NiO calculated in GGA (Ref. 20), LDA+ U (Ref. 20), and LDA+DMFT(QMC) (Ref. 21) approaches to $O K\alpha$ XES and $O 1s$ XAS of NiO.

tra is proposed and implemented, and the values produced very closely agree with previously published results. Combining XES and TFY XAS measurements is shown to provide a bulk-sensitive representation of the DOS, which can be used to evaluate the effectiveness of numerical structural methods. A major strength of this experimental method is that the measurements are quite simple and can be performed on commercially available materials without the need for extensive surface preparations.

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