

Electronic structures of α -Fe₂O₃ and Fe₃O₄ from O *K*-edge absorption and emission spectroscopy

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We present O *K*-edge absorption and emission spectra for α -Fe₂O₃ and Fe₃O₄ obtained using a high-resolution-undulator soft-x-ray radiation source. The occupied and the unoccupied O *p* densities of states are obtained and compared with the valence-band photoemission results. While these results confirm that α -Fe₂O₃ can be classified as a charge transfer or an intermediate-type insulator, they suggest that Fe₃O₄ is more likely of the Mott-Hubbard type. The excitation-energy dependence of the emission spectra is also discussed.

Since the discovery of high-temperature superconductivity in the doped cuprate oxides the electronic structure of transition-metal oxides has attracted renewed attention. While many of their unique properties are attributable to the importance of the correlation effects among the transition-metal *3d* electrons, the hybridization between these *3d* states and the bandlike O *2p* states played an essential role in determining the nature of the insulator gap. According to Zaanen, Sawatzky, and Allen,¹ earlier transition-metal oxides are Mott-Hubbard insulators, while late transition-metal oxides, e.g., Ni and Cu oxides, are of the charge-transfer type. Iron oxides are believed to be at the borderline of the two regimes. Consequently, Fe_xO, α -Fe₂O₃, and Fe₃O₄ have been extensively investigated by computational and experimental techniques. It has been suggested that they are charge-transfer insulators.²⁻⁷

Much of our current understanding on this subject is based on the experimental valence-band photoemission results.²⁻⁵ Using synchrotron radiation, resonant photoemission techniques have been used to obtain the separate contributions to the valence-band density of states due to individual elements, i.e., iron and oxygen. However, the separation is not straightforward, especially when there is strong hybridization between the Fe *3d* and the O *2p* orbitals. For example, there have been several conflicting estimates of the O *2p* bands for these iron oxides.^{2,4,5} Yet the positions of the O *2p* bands are essential to the nature of the insulator state: if the states on both sides of the band gap are of Fe *3d* character, the material is of the Mott-Hubbard type because the conduction is dominated by the correlation energy of the *3d* electrons. Otherwise,

they belong to the charge-transfer regime because the gap is formed from the charge transfer between Fe and O atoms. In this paper we use a more direct method to probe the O *p* bands, i.e., the O *K*-edge absorption and emission spectra, which probe the unoccupied and occupied O *p* density of states, respectively. By comparing with the total valence-band density of states obtained from photoemission measurements, the nature of the states in the neighborhood of the band gap can be identified. For α -Fe₂O₃, the O *2p* emission resembles that of the Fe *3d* photoemission spectrum, indicating strong hybridization in the valence-band region and confirming that it is not a Mott-Hubbard-type insulator. On the other hand, the O *2p* density of states of Fe₃O₄ shows differences from the *3d* photoemission results, especially near the top of the valence band. This can be attributed to the presence of the Fe²⁺ (*d*⁶) ion in this compound. Therefore, contrary to recent suggestions,^{4,5} the highest occupied state is of Fe *d*⁶ origin and Fe₃O₄ is better described as of the Mott-Hubbard type.

The emission spectra reported in this paper were obtained with high-resolution monochromatic photon energy excitation. By tuning the excitation energy to just above the O *K* edge, we obtained clean O *K*-emission spectra that are free of satellites usually associated with high-energy electron excitation. The experiment was performed at the beamline X1B of the National Synchrotron Light Source. The beamline, using the X1 undulator and spherical grating monochromator, provides intense high-resolution soft-x-ray radiation.⁸ The excitation photon bandpass was set to 0.5-0.7 eV at energies of approximately 540 eV. The O *K*-edge emission spectra were

measured using a high-resolution grazing incidence multigrating spectrometer with a two-dimensional detector.⁹ The emission spectra presented in this paper were taken with the spectrometer resolution set to about 1.5 eV. Both the absorption and emission spectra have also been measured with higher resolution. No noticeable difference was observed. The *K*-edge absorption spectra were obtained using the fluorescence yield method. They are similar to the electron yield results of Ref. 10 after *in situ* scraping of the sample surface. Calibration of the photon energy in the emission spectra was done by the *L*-edge emission of Cr metal, while the absorption spectra are aligned to those of Ref. 10. Because of the two different methods, the overall photon calibration could be off by 0.2–0.3 eV. The single-crystal samples were oriented so that the incident photon is 70° from the surface normal direction.

The O *K*-edge absorption and emission spectra for α -Fe₂O₃ and Fe₃O₄ are shown in Figs. 1 and 2, respectively. The absorption spectra are the subject of a recent study by de Groot *et al.*¹⁰ They have identified the features in the spectra as transitions from the O 1s to unoccupied states resulting from O 2p and Fe 3d–4s hybridization. In particular, the O 2p–Fe 3d hybridized state has mostly 3d character and is split into *t*_{2g} and *e*_g states by the ligand field. These are the peaks at 529.4 (*t*_{2g}) and 530.7 (*e*_g) eV for α -Fe₂O₃. For Fe₃O₄ the situation is more complicated because the Fe³⁺ ions occupy both tetrahedral and octahedral sites where the *e*_g and *t*_{2g} states are split in the opposite directions by the crystal fields. In addition, for the Fe²⁺ species the *d*⁶ multiplets contribute a complicated structure in this region. Consequently, the peak at around 528.5–531 eV can only be identified as a mixture of *e*_g and *t*_{2g} states as well as the *d*⁶ multiplets. It was also suggested that the structure in the region from 532 to about 542 eV reflected the hybridization of C 3p and Fe 4sp states.

The O *K*-emission spectra were obtained at several excitation energies indicated in the figures. Since the O *K*-emission probes the O 2p contribution of the valence band, it is seen that the maximum of the 2p band is at about 5 eV from the top of the valence band for both

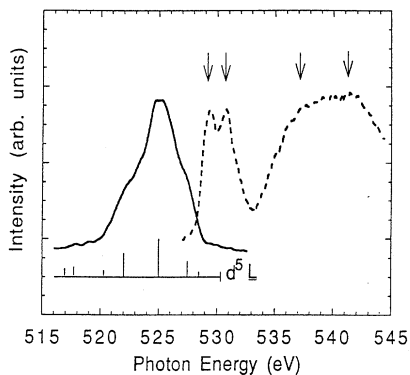


FIG. 1. O *K*-edge absorption (dashed) and emission (solid) spectrum of α -Fe₂O₃. The arrows indicate the excitation energies of the photon used in obtaining the emission spectra. The vertical lines indicate the result of the CI calculations of Ref. 3.

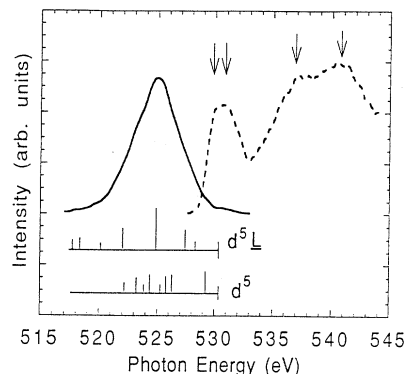


FIG. 2. O *K*-edge absorption (dashed) and emission (solid) spectrum of Fe₃O₄. The vertical lines indicate the result of the CI calculations of Ref. 2.

crystals. The widths of the 2p bands are also similar, about 10 eV wide. These observations are in agreement with those estimated from resonant photoemission experiments.⁵ For α -Fe₂O₃, shoulders on both sides of the main peak, at about 8 and 3 eV from the top of the valence band, can be seen. They are not well resolved in the O 2p photoemission results.⁵ These features are not as clear for Fe₃O₄. In particular, it appears that there is no shoulder at 3 eV below the valence-band maximum.

To understand the implications of these results, we compare the emission spectra with the total density of states obtained from photoemission experiments and configuration-interaction (CI) FeO₆ cluster calculations. For α -Fe₂O₃ we notice substantial similarities between x-ray photoemission spectroscopy (XPS) spectra,^{2–5} the soft-x-ray emission spectrum, and the 3d⁵L final-state CI results,^{2,3} also shown in Fig. 1. The main peak and the shoulders can all be identified with the features of the 3d⁵L state. On the other hand, the emission spectrum also resembles the Fe *L* α emission spectrum, which directly probes the Fe 3d derived states.⁶ Because of this strong similarity, we conclude that, for α -Fe₂O₃, the top of the valence band results from strongly hybridized O 2p and Fe 3d orbitals. This is in agreement with previous conclusions from XPS studies.^{2–6} However, our method, using the element and orbital symmetry specific x-ray emission, directly probes the orbitals in question. In the oxides, the ligand orbitals are mostly of O 2p character; O *K* emission has the same final state as that of the well-screened 3d photoemission. Therefore the O *K*-emission technique has the unique advantage of directly probing the 3d^{*n*}L final state of the system. These observations suggest that α -Fe₂O₃ is a charge transfer or an intermediate insulator, in agreement with previous conclusions.^{2–6}

For Fe₃O₄, Fig. 2 shows that the *K*-emission spectrum has a different shape than that of the valence-band XPS.⁵ The main peak is still at about 5 eV, but the shoulders have disappeared when compared with the spectrum from α -Fe₂O₃, particularly near the top of the valence band. We note that the XPS peak observed at 1.2 eV (Refs. 2, 4, and 5) must be of mostly Fe 3d character because it is not observed in the O 2p bands. Indeed, CI

calculations have associated this peak to that of the $3d^5$ photoemission final state of the Fe⁺² ion (which has $3d^6$ configuration in the ground state).² Thus for this case, the states at both sides of the energy gap are of Fe $3d$ origin. This suggests that, unlike α -Fe₂O₃, Fe₃O₄ should be classified as a Mott-Hubbard "insulator"¹¹ with an energy gap dominated by the correlation energy of the Fe $3d$ electrons. The reason for the difference is due to the presence of the Fe⁺² ions in this compound which, in the $3d^6$ configuration, is relatively easily ionized, thereby yielding a half-filled d shell.¹² Based on the same argument and the experimental results of Galakhov *et al.*,⁷ Fe_xO should also be considered as a Mott-Hubbard insulator.

Finally, we comment on the excitation-energy dependence of the emission spectra. The emission spectra were taken at several excitation energies indicated in Figs. 1 and 2. Within the experimental statistics, no significant excitation-energy dependence is observed for both the α -Fe₂O₃ and Fe₃O₄. This is noteworthy because at different energies the photoelectrons are excited into different orbitals. In the case of excitation into the t_{2g} and e_g states that resulted from the hybridized states of $d^6\bar{L}$, the initial state of the emission process has d^6 configuration. The photoelectron is highly localized. At higher excitation energies, the photoelectron is excited to O $3p$ -Fe $4sp$ hybridized states that are more delocalized. It is interesting that the photoelectron did not affect the multiplet struc-

ture of the valence bands, which indicates that the extra d electron did not affect the hybridization of the Fe d^5 configuration.

In summary, the O $2p$ derived states of α -Fe₂O₃ and Fe₃O₄ have been studied by soft-x-ray absorption and emission spectroscopy. The O K -edge spectra, in combination with photoemission results and cluster calculations, provided a clear picture for the nature of the electronic states near the band gap in both oxides. These results confirmed that α -Fe₂O₃ is a charge transfer or intermediate insulator but suggest that Fe₃O₄ is of the Mott-Hubbard type. The use of monochromatic photon excitation in obtaining the emission spectra eliminated the usual problem associated with the electron-beam excitation, such as sample damage and multivalence satellite structure. This work demonstrated that, because of its unique characteristics, such as element and orbital specificity, bulk sensitivity, and absence of sample charging problem, x-ray absorption and emission spectroscopy can be very useful in elucidating the electronic properties of transition-metal compounds.

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