Oxygen 1s x-ray-absorption edges of transition-metal oxides

F. M. F. de Groot, M. Grioni, and J. C. Fuggle
Research Institute for Materials, University of Nijmegen, Toernooiveld, NL-6525 ED Nijmegen, The Netherlands

J. Ghijsen and G. A. Sawatzky
Materials Science Centre, University of Groningen, Paddepoel, Nijenborgh 18, NL-9747 AG Groningen, The Netherlands

H. Petersen
Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY), Lentzeallee 100,
D-1000 Berlin 33, Federal Republic of Germany
(Received 17 February 1989; revised manuscript received 8 May 1989)

The oxygen 1s x-ray-absorption edges of a series of 3d-transition-metal oxides have been measured. The structures at the edge arise from covalent mixing of the metal and oxygen states, which introduces oxygen p character in unoccupied states of mainly metal character. The spectra can be divided into two regions: The first is a double-peaked sharp structure near threshold, which can be related to the metal 3d states; the second is a broader structure 5–10 eV above the edge and is related to the metal 4s and 4p bands. We attribute the oxygen p character up to 15 eV above threshold to mainly oxygen 2p character. The data are analyzed in terms of ligand-field and exchange splittings. It is shown that the splitting between the two sharp peaks near threshold is related closely to the ligand-field splitting, but the relative intensities of the peaks are not fully explained at the present time.

I. INTRODUCTION

In this study we try to learn something about the electronic structure of binary 3d-transition-metal oxides, which still is not well understood despite many past studies. By studying the oxygen 1s (or K) absorption edge of binary oxides, we hope to set up a reference for the interpretation of x-ray-absorption edges and the electronic structure of more complex compounds, such as the high-Tc superconducting oxides. The oxygen 1s edge, with an absorption energy of about 530 eV, is situated in the energy range between 300 and 1000 eV, which until recently was technically difficult to reach. The relatively underdeveloped role of this energy region, containing besides the oxygen 1s edge also the 3d–transition-metal 2p (or L2,3) edges, compared to, e.g., the transition-metal 1s (or K) edges is predominantly caused by poor monochromator resolution. Studies such as ours, with an instrumental resolution of ~500 meV, are now feasible as a result of the development of new and better monochromators for synchrotron radiation in this energy range.

X-ray absorption (XAS) is a local process in which an electron is promoted to an excited electronic state, which can be coupled to the original core level with the dipole selection rule stating that the change in the angular momentum quantum number (ΔL) is ±1, while the spin is not changed. For the oxygen 1s edge (L = 0) this means that only oxygen p character (L = 1) can be reached. The resulting spectrum can be envisaged in a first-order approximation as an image of the oxygen p projected unoccupied density of states. For more detailed studies, we note below three problems in relating a calculated DOS to an XAS spectrum.

First, the usual way to calculate the density of states is via the Hohenberg-Kohn density-functional theory within the Kohn-Sham local-density approach (LDA). Using the LDA, the occupied part of the DOS calculation is a routine task for the 3d-transition-metal oxides. For the unoccupied states there are, however, purely technical problems of the requirements for more extended basis sets and avoidance of inappropriate linearization schemes. For instance, the O 3p levels, which begin 10–15 eV above E_F, are not included in density-of-states (DOS) calculations with a basis set limited to one wave function per L value. Thus, most published calculations are limited to the first few eV of the unoccupied states. Unfortunately, we know of only one oxide band-structure calculation (for CuO) (Ref. 13) whose basis set is sufficient for a sensible comparison with XAS far above threshold. Calculations also exist within the multiple-scattering formalism which treat the unoccupied density of states (UDOS) up to some 50 eV above threshold. However, these calculations, which are used in the description of the transition-metal 1s x-ray-absorption near-edge spectroscopy (XANES) spectra, have not been published for the oxygen 1s edges of many of the oxides we consider here. A second technical problem concerns the single-particle matrix elements for XAS. Here we will assume that the oxygen 1s → np matrix elements are constant for any given n unless otherwise stated.

Finally, there is an important problem of principle. Even if the UDOS was calculated correctly within LDA and corrected for single-particle matrix elements, a comparison to the x-ray-absorption edges is not strictly valid. The excited electron in the final state interacts with its surroundings, modifying the density of states due
to correlation. Moreover, the created core hole affects the final-state DOS, as has, for instance, been shown for the early-transition-metal 2p (L_{2,3}) (Ref. 16) and Al and Si 1s (Ref. 17) x-ray-absorption spectra. Both effects come under the heading of self-energy. For the oxygen 1s edges these effects probably are less severe, compared to the transition-metal 2p edges, because the core hole now is situated on oxygen while the states in the unoccupied bands just above the Fermi level have most weight on the metal sites. Oxygen 2p character hybridizes with these unoccupied metal bands, but the 1s hole on oxygen only indirectly influences them.

Because not much high-resolution data are available, and even more because of the lack of suitable calculations of the UDOS, we confine ourselves here to a more empirical approach as a starting point. In this paper we study a series of 3d-transition-metal oxides, of which all but one (CuO) contain a transition metal which is octahedrally surrounded by oxygen. The major variation is the number of 3d electrons, ranging from zero to nine. Also the formal valency varies between 2 and 4, resulting in different crystal structures for each valency: Sc2O3, TiO2, V2O5, Cr2O3, and Fe2O3, each with the corundum structure; TiO2, VO2, and MnO2, each with the rutile structure and the complex inverse spinel-structures Fe2O4. We also consider the spectra of the monoxides TiO, MnO, FeO, NiO, and CuO of Nakai et al. The first four materials have the rocksalt structure and CuO has its typical structure in which Cu is surrounded by four oxygen atoms. The measurements on NiO and CuO were repeated by us to check the reproducibility of the results under different experimental conditions. We note that especially the monoxides discussed are defect structures, defects can have a considerable influence on XAS spectra as they distort the local symmetry. Besides the known defect structures of the monoxides, the samples measured as commercial powders (see Sec. II) can be expected to contain a fair amount of defects. As a start we will consider all compounds as stoichiometric; the possible effects of nonstoichiometry are discussed in Sec. IV.F.

After a short description of the experimental conditions (Sec. II), we will present the oxygen 1s edges. In their interpretation we will focus on the transition-metal 3d-band region (Sec. III). In the discussion (Sec. IV) a comparison is made with the ligand-field-splitting data from the literature and simple models to explain the specific shapes of the 3d-band region are discussed.

II. EXPERIMENTAL

The x-ray-absorption measurements were carried out at the Berlin synchrotron-radiation source BESSY, using the SX700 plane-grating monochromator. The contribution to the resolution could be reasonably simulated by a Lorentzian of about 0.5 eV full width at half maximum (FWHM). However, it should be noted that our spectra show as much detail as those of Nakai et al., who claims 0.1 eV monochromator resolution. The spectra were recorded in the total-electron-yield mode. They were normalized to the beam current, to correct for synchrotron-intensity loss during a measurement. The samples used were commercial powders (Sc2O3, TiO2, VO2, V2O5, and Cr2O3) and natural minerals (TiO2, MnO2, MnO, Fe2O3, Fe3O4, and NiO). CuO was obtained as a single crystal from Oxford Laboratories. Solid samples were scraped under vacuum to ensure clean surfaces and were thus preferred to powders. The pressure during measurements was in the 10−7 torr range.

The throughput of Cu was measured at the oxygen 1s edge to check for oxygen contamination in the monochromator. No contamination was found. The energy calibration of the monochromator was performed by taking pure transition metals (V, Cr, Mn, Fe, and Ni) 2p edges and using the energy-loss data of Fink et al. as a reference. The calibration curve was linear in the energy range probed (400–800 eV). Comparing our numerical results for NiO and CuO with those of Nakai et al. showed in both cases that our threshold was shifted 0.3 eV to higher energy, which at this time is an acceptable disagreement for these XAS edges.

III. RESULTS AND INTERPRETATION

Figures 1(a) and 1(b) show the oxygen 1s edge x-ray-absorption spectra of a series of 3d-transition-metal oxides. The spectra have been approximately normalized to the peak heights; absolute normalization of the intensity scale is not feasible. The spectra have strong structure up to at least 15 eV above threshold and it is this structure we wish to interpret. First, we note that the data presented here are in good agreement with the high-resolution data that exist for TiO2 (Ref. 22) and for NiO and CuO. There is also no disagreement with the available lower-resolution spectra. Besides the oxygen 1s edge data there are results on the metal edges of 3d-transition-metal oxides. These are significant for a complete picture of the electronic structure. However, in this paper we do not include the discussion of the metal edges and consider only the oxygen 1s edge.

We divide the spectra into two regions. The first, shaded in the figures, is attributed to oxygen 2p weight in states of predominantly transition-metal 3d character: the transition-metal 3d band. This assignment conforms with that of Fisher and other studies, based on a molecular-orbital treatment. Further discussion of this region is given in Sec. IV.

The second region, typically 5–10 eV above threshold, is attributed to oxygen 3p character hybridized with metal 4s and 4p states. Detailed calculations on CuO with an extended basis set (with the inclusion of both oxygen 2p and 3p character) show this to have principally oxygen 2p (not 3p) character, with the 2p count reaching ~6 at about 15 eV above EF. We proceed under the assumption that the peaks up to about 15 eV in the other transition-metal oxides are also due to oxygen 2p character in the unoccupied states. This high-energy range of spread for oxygen 2p character is an indication of strong covalency in these materials and is not in disagreement with traditional chemical ideas. From Fig. 1 and Table I a common structure of the 4sp band, consisting of a main peak (Ep) and a low-energy shoulder (Ep−1) at approximately 3.2 eV (Δp), appears throughout the series.
This structure can be related to the \( O_{1s} \) symmetry set up by the nearest (oxygen) neighbors, which octahedrally surround the 3d-transition-metal atoms. It shows no strong dependence on the specific crystal structure. This structure is absent in the nonoctahedral CuO.

A salient point is the decrease in intensity of the 3d band, relative to the 4sp band across the transition-metal series (see Fig. 2). As noted above, the dominant reason for this is the decrease in the number of unoccupied 3d states available for mixing with O 2p states; this means that the intensity of the XAS spectra should be linear with the number of holes as is indicated by the line in Fig. 2. However, there is a substantial lower intensity of the 3d-band region, especially for the \( d^5 \) and \( d^6 \) oxides. This additional loss of intensity can be explained by the diminished hybridization of the metal 3d orbitals with the oxygen 2p orbitals due to shrinking of the metal 3d orbitals in the late-transition-metal oxides. Note that we have plotted the relative intensity of the 3d region with respect to the 4sp region. The intensity of this latter region also will be influenced by hybridization. We can say something more about the changes in hybridization in the 3d and 4s bands with the use of the hybridization strengths (\( \Delta \) values) from Andersen et al.\(^{32} \) For all transition metals they give tables of the \( \Delta \) values of each individual \( l \) band (\( l=0,1,2,3 \)). This \( \Delta \) value, a potential parameter in the linear muffin-tin orbital (LMTO) calculation, is proportional to the amplitude of the corresponding radial wave function at the average Wigner-Seitz radius of the lattice. The hybridization is equal to \( \Delta^{1/2} \), which gives a direct relation between \( \Delta \) and the intensity of the 3d and 4s bands. The values for the pure metals give a clear and—except for titanium—monotone trend to smaller 3d versus 4s hybridization with a higher atomic number. Using these (metal) values for the oxides, we have to multiply the number of holes (the straight line in Fig. 2) by \( \Delta_{3d}/\Delta_{4s} \) and renormalize the plot. We find that the experimental points are scattered around the resulting curve. This indicates strongly that the additional

\[ \text{FIG. 1. (a) and (b) Oxygen 1s x-ray-absorption spectra: the shaded area is assigned to oxygen } p \text{ character in the transition-metal 3d band. The broader structure above is assigned to oxygen } p \text{ character in the metal 4s and 4p bands. The vanadium edges are distorted by the tail of the vanadium } L_2 \text{ edge.} \]

\[ \text{FIG. 2. The intensity of the 3d-band region with respect to the 4sp region is plotted against the number of 3d electrons in the ground state. The intensity of TiO}_3\text{ is set to 10. The line gives the expected intensity ratio, assuming this is proportional to the number of holes.} \]
loss of intensity can be explained by taking into account hybridization of both the 3d and 4s bands. (The curve itself is not included in order not to mislead the reader; a complete treatment would involve calculation of the Δ's for the oxides.)

IV. DISCUSSION

A. Implication of the O 1s XAS for Ideas on Covalency

In a purely ionic model, oxygen would have the configuration O 1s^2 2s^2 2p^6 and the 1s→2p channel would be closed in XAS. Covalency reduces the number of filled states with O 2p character, so that the strength of the O 1s signal at threshold is related to the degree of covalency. It is well known that the transition-metal oxides are not ionic, but have a considerable covalent contribution. There is much evidence for this from pure computations as well as from comparison of computed and experimental magnetic or ligand-field effects. It is of particular interest that the ligand-field splittings calculated for early-transition-metal oxides in an ionic model (the crystal field) are about a factor of 3 smaller than those found by optical measurements, but come out correctly when covalency is taken into account. The discrepancies are smaller in the late-transition-metal oxides, which is extra evidence that the (oxygen 2p→metal 3d) hybridization is smaller in the late-transition-metal

TABLE I. (a) The crystal structures, formal valencies, and number of d electrons are given. From the spectra in Fig. 1 and from Ref. 19 the first (E_d1) and second (E_d2) peak positions of the 3d band (shaded area) and the first (E_p1) and second (E_p2) peak positions of the 4p band are measured. (b) The peak splittings and widths of the oxygen 1s XAS spectra: the separation of E_d1 and E_d2 is identified with the ligand-field splitting (Δd). The characteristic 3.2-eV distance between E_α and E_β in the sp band is given as Δp. The left-side HWHM(Δ) of the first peak (Γ_E), the FWHM of the total 3d band (Γ_σ), and the FWHM of the 4p band (Γ_p) are given. The O 1s edges in VO_2 are distorted by the tailing effect of the vanadium L edges. We estimate the uncertainty in Γ_p as ±0.3 eV. All energies are in eV.

(a)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal structure</th>
<th>Valency</th>
<th>d count</th>
<th>E_d1</th>
<th>E_d2</th>
<th>E_p1</th>
<th>E_p2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc_2O_3</td>
<td>corundum</td>
<td>3+</td>
<td>0</td>
<td>532.4</td>
<td>535.7</td>
<td>539.4</td>
<td>543.1</td>
</tr>
<tr>
<td>TiO_2</td>
<td>rutile</td>
<td>4+</td>
<td>0</td>
<td>530.7</td>
<td>533.2</td>
<td>539.0</td>
<td>542.7</td>
</tr>
<tr>
<td>Ti_2O_3</td>
<td>corundum</td>
<td>3+</td>
<td>1</td>
<td>530.8</td>
<td>533.2</td>
<td>539.0</td>
<td>542.2</td>
</tr>
<tr>
<td>TiO^4</td>
<td>rocksalt</td>
<td>2+</td>
<td>2</td>
<td>530.2</td>
<td>533.0</td>
<td>539.5</td>
<td>542.5</td>
</tr>
<tr>
<td>VO_2</td>
<td>rutile</td>
<td>4+</td>
<td>1</td>
<td>528.8</td>
<td>531.0</td>
<td>540.4</td>
<td>543.1</td>
</tr>
<tr>
<td>V_2O_5</td>
<td>corundum</td>
<td>3+</td>
<td>2</td>
<td>529.8</td>
<td>531.9</td>
<td>539.2</td>
<td>542.8</td>
</tr>
<tr>
<td>Cr_2O_3</td>
<td>corundum</td>
<td>3+</td>
<td>3</td>
<td>531.4</td>
<td>533.7</td>
<td>538.4</td>
<td>542.7</td>
</tr>
<tr>
<td>MnO_2</td>
<td>rutile</td>
<td>4+</td>
<td>3</td>
<td>528.9</td>
<td>531.4</td>
<td>540.5</td>
<td>543.4</td>
</tr>
<tr>
<td>MnO^4</td>
<td>rocksalt</td>
<td>2+</td>
<td>5</td>
<td>529.6</td>
<td>530.9</td>
<td>538.4</td>
<td>542.5</td>
</tr>
<tr>
<td>Fe_2O_3</td>
<td>corundum</td>
<td>3+</td>
<td>5</td>
<td>529.4</td>
<td>530.7</td>
<td>537.4</td>
<td>540.6</td>
</tr>
<tr>
<td>Fe_2O_4</td>
<td>inverse spinel</td>
<td>2+ and 3+</td>
<td>5 and 6</td>
<td>528.9</td>
<td>530.5</td>
<td>537.1</td>
<td>540.2</td>
</tr>
<tr>
<td>FeO^4</td>
<td>rocksalt</td>
<td>2+</td>
<td>6</td>
<td>529.8</td>
<td>531.0</td>
<td>536.3</td>
<td>540.2</td>
</tr>
<tr>
<td>NiO</td>
<td>rocksalt</td>
<td>2+</td>
<td>8</td>
<td>531.7</td>
<td>537.0</td>
<td>540.2</td>
<td>540.2</td>
</tr>
<tr>
<td>NiO^4</td>
<td>rocksalt</td>
<td>2+</td>
<td>8</td>
<td>531.4</td>
<td>536.7</td>
<td>540.0</td>
<td>540.0</td>
</tr>
<tr>
<td>CuO</td>
<td>CuO</td>
<td>2+</td>
<td>9</td>
<td>530.1</td>
<td>534.6</td>
<td>535.9</td>
<td>535.9</td>
</tr>
<tr>
<td>CuO^4</td>
<td>CuO</td>
<td>2+</td>
<td>9</td>
<td>529.8</td>
<td>534.3</td>
<td>535.6</td>
<td>535.6</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Gamma_E) HWHM(Δ)</th>
<th>(\Gamma_P) FWHM</th>
<th>(\Gamma_P) FWHM</th>
<th>Δd</th>
<th>Δp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc_2O_3</td>
<td>0.8</td>
<td>6.0</td>
<td></td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>TiO_2</td>
<td>1.0</td>
<td>4.8</td>
<td>9.5</td>
<td>2.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Ti_2O_3</td>
<td>1.2</td>
<td>5.3</td>
<td>9.1</td>
<td>2.4</td>
<td>3.2</td>
</tr>
<tr>
<td>TiO^4</td>
<td>0.6</td>
<td>5.3</td>
<td>9.1</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>VO_2</td>
<td>0.9</td>
<td>4.9</td>
<td>7.6</td>
<td>2.2</td>
<td>2.7</td>
</tr>
<tr>
<td>V_2O_5</td>
<td>1.0</td>
<td>4.9</td>
<td>6.5</td>
<td>2.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Cr_2O_3</td>
<td>0.9</td>
<td>3.6</td>
<td>7.3</td>
<td>2.3</td>
<td>4.3</td>
</tr>
<tr>
<td>MnO_2</td>
<td>0.9</td>
<td>4.2</td>
<td>8.5</td>
<td>2.5</td>
<td>2.9</td>
</tr>
<tr>
<td>MnO^4</td>
<td>0.6</td>
<td>3.7</td>
<td>7.8</td>
<td>1.3</td>
<td>4.1</td>
</tr>
<tr>
<td>Fe_2O_3</td>
<td>0.7</td>
<td>3.3</td>
<td>8.4</td>
<td>1.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Fe_2O_4</td>
<td>0.8</td>
<td>3.0</td>
<td>7.1</td>
<td>0.9</td>
<td>3.1</td>
</tr>
<tr>
<td>FeO^4</td>
<td>0.8</td>
<td>3.8</td>
<td>6.8</td>
<td>1.2</td>
<td>3.3</td>
</tr>
<tr>
<td>NiO</td>
<td>0.7</td>
<td>2.3</td>
<td>6.7</td>
<td></td>
<td>3.2</td>
</tr>
<tr>
<td>NiO^4</td>
<td>0.6</td>
<td>2.0</td>
<td>5.6</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>CuO</td>
<td>0.6</td>
<td>1.4</td>
<td>3.2</td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>CuO^4</td>
<td>0.45</td>
<td>1.1</td>
<td>3.3</td>
<td></td>
<td>1.3</td>
</tr>
</tbody>
</table>

*Data taken from Reference 19.
oxides, as we already suggested in the discussion of the intensities of the 3d band throughout the series.

Because of the technical problems in computing the unoccupied DOS over some energy range, it is not always realized that there is considerable weight of O 2p character in states 10–15 eV above \( E_F \). The evidence from the LASSW calculation of CuO is that most O p character up to 15 eV above \( E_F \) is in fact O 2p.\textsuperscript{13} The O 1s XAS spectra of the transition-metal oxides show similar broad peaks, which we have attributed to O 2p character in bands with predominantly transition-metal 4sp character. We note that the integrated intensity of the broad 4sp band is comparable to that of the 3d band. In the very reasonable first approximation of constant O 1s → 2p matrix elements, the XAS intensity is proportional to the weight of O 2p character in a band. Thus, in chemical language, the observed intensity ratios in the two spectral regions is evidence that, besides the metal 3d states, also the metal 4sp states are important for the covalency of transition-metal oxides.

B. Ligand-field splittings

We now examine more closely the first structure, the 3d band, which is shaded in Fig. 1. This structure consists of two (often similar) peaks. In a first approximation these two peaks can be identified as the \( t_{2g} \) and \( e_g \) symmetry bands separated by a ligand-field splitting; we shall use the term “ligand-field splitting” to denote the “bare” (ionic) crystal-field splitting plus hybridization.\textsuperscript{36}

To check the validity of the assignment of the two sharp peaks as being related to the \( t_{2g} \) and \( e_g \) symmetry, with the peak separation mirroring the ligand-field splitting, we first compare our splittings, \( \Delta d \), with optical data of octahedrally hydrated transition-metal ions, which have been related to the ligand-field splitting.\textsuperscript{5,7} In this comparison some precautions must be taken. Obviously the materials compared are not identical, though in both cases the transition metal is octahedrally surrounded by oxygen ions. Bearing this in mind we compare the results for the ligand-field splitting which are tabulated in Table II. Considering the precision in the determination of our \( \Delta d \) value, good agreement is found for all five transition-metal oxides.

In contrast to the “general rule” that the ligand-field splitting of trivalent ions is around 2.5 eV and the divalent-ion ligand-field splitting is approximately half that value,\textsuperscript{9} we come to the generalization of the division of early- and late-transition-metal oxides, the early-transition-metal oxides with a splitting around 2.5 eV and the late-transition-metal oxides with a splitting round 1.2 eV, as can be checked in Table I. The dividing line between early- and late-transition-metal oxides is the presence of a filled \( e_g \) orbital in the ground state. Up to \( d^3 \) compounds only \( t_{1g} \) states are filled. From \( d^5 \) compounds the filled \( e_g \) states increase the lattice parameter with respect to the orbital radii, which decrease throughout the 3d-transition-metal series. The consequence for the 3d orbitals is a decrease of hybridization as we discussed in Sec. III. The \( d^4 \) compounds fall in between the early- and late-transition-metal compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta d )</th>
<th>LFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2}</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>V\textsubscript{2}O\textsubscript{3}</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Cr\textsubscript{2}O\textsubscript{3}</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>MnO</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>1.3</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Despite the “disagreement” in the generalizations made, the good individual correspondences of \( \Delta d \) with the optical ligand-field-splitting data give us confidence that the splitting between the two peaks in the 3d band is the same as that attributed to the ligand-field splitting in optical spectra.

C. The intensities of the so-called \( t_{2g} \) and \( e_g \) peaks

XAS data on peak splittings are analogous to those given by optical-absorption spectroscopy, except that XAS can more easily be used for \( d^0 \) materials. However, oxygen 1s XAS spectra also contain information on the peak intensity ratios, which have no analogy in optical data, and in fact our analysis of these intensities will indicate a serious problem, and possibly the need to revise the assignment somewhat. We will develop the ideas of the peak intensities step by step.

The simplest and first effect to be taken into account is the electron counting. The \( t_{2g} \) orbitals \((xy, xz, z^2)\) can take six electrons and the \( e_g \) orbitals \((x^2−y^2, z^2)\) can take four. Thus the ratio of empty orbitals \( t_{2g}: e_g \) is 6:4 for \( d^0 \) compounds and decreases to zero in low-spin compounds as the electron count is increased to \( d^6 \). This is shown by the dashed line in Fig. 3. However, note that for high-spin materials the exchange splitting may lead to filling of the majority-spin \( e_g \) states before the minority-spin \( t_{2g} \) states. Thus for high-spin compounds the ratio of \( t_{2g}: e_g \) holes rises from 3:4 at \( d^3 \) to 3:2 at \( d^5 \), before dropping to 0:2 at \( d^6 \), as is shown by the upper dashed line in Fig. 3. The curves based on electron counting in Fig. 3 may be compared with the experimental ratio of the first to second peaks. Although the separation of the two peak areas is only approximate, we immediately see some serious discrepancies. There is considerable scatter of the experimental points, which may be an indication of the accuracy of the separation, but for the \( d^1 \) materials Cr\textsubscript{2}O\textsubscript{3} and MnO\textsubscript{2} the ratio of the low-energy to the high-energy peak is much too high to be explained by ideas based on electron counting.

D. Orbital hybridization

We note that even where the peak intensity ratio is in reasonable agreement with the electron-count curve, this creates a problem because of the role of orbital hybridization. In octahedral complexes the metal \( e_g \) orbitals are directed towards the oxygen atoms and have a stronger overlap with the oxygen 2p orbitals. In general it is assumed\textsuperscript{1} (following calculations\textsuperscript{6,38,39}) that the hybridiza-
we must consider exchange effects, which split the two groups of bands, \( t_{2g} \) and \( e_g \), into four: spin-up \( t_{2g} \), spin-up \( e_g \), spin-down \( t_{2g} \), and spin-down \( e_g \). Consider, for example, the \( d^3 \) compounds \( \text{Cr}_2\text{O}_3 \) and \( \text{MnO}_2 \), which show a sharp peak near threshold followed by a weak shoulder at 2.4 eV. This result can only be explained if exchange is included. The exchange splitting is proportional to the number of unpaired spins, being three in \( d^3 \) compounds. For \( \text{Cr}^{3+} \) the tabulated exchange splitting per spin is about 0.9 eV. The total splitting becomes 2.7 eV, which is about the same value as the ligand-field splitting (=2.3 eV). Including this exchange splitting makes the approach to the spectrum quite different. Looking at the spectrum (see also Fig. 4), the first peak can be assigned to a superposition of the spin-down \( t_{2g} \) state and the spin-up \( e_g \) state with a total number of five electrons. The second peak (shoulder) relates to the remaining two spin-down \( e_g \) electrons. This superposition is thus a consequence of the equivalent values of exchange and ligand-field splitting.

The result of including exchange effects here is that the electron-counting method increases the peak ratio to 5(3+2):2. If hybridization is included with a factor of 2, as in Sec. IV D, this value is still only decreased to (3+2):1 = 1.7. It is clear that a value of the \( t_{2g}\) hybridization ratio could be chosen so as to fit the experimentally observed peak ratio. We conclude on the basis of this analysis for \( d^3 \) compounds that exchange effects should not be ignored. However, there are other compounds with other numbers of \( d \) electrons for which exchange splittings cannot explain the discrepancies in Fig. 3. An example are the high-spin \( d^3 \) compounds \( \text{MnO} \) and \( \text{Fe}_2\text{O}_3 \).

In oxygen 1s absorption, an electron is excited from the oxygen 1s core state to states with some oxygen \( p \) character, i.e., \( |t_{2g}\rangle, |e_g\rangle \). Thus we can now relate the intensities to the covalency: \( n, \alpha_1^2 \) gives the amount of \( |t_{2g}\rangle \) character in the ground state and it is this character which is probed in the oxygen 1s absorption process. From this it is clear that the intensity ratio \( I_e/I_s \) should be equivalent to the amount of covalent mixing \( n, \alpha_1^2 / n, \alpha_2^2 = n_1 / n_2 \). In Fig. 3 we have compared this ratio (solid line) to the experimental values. It is directly evident that the theoretical lines strongly underestimate the experimental ratio, i.e., the relative \( t_{2g} \) intensity. At this moment we cannot explain the relative intensities generally observed, despite consideration of several subsidiary effects described below.

### E. Exchange splitting

The whole concept of high-spin and low-spin configurations for 3d-transition-metal oxides implies that...
for which the energy levels are illustrated in Fig. 5. The exchange splitting is much larger than the crystal-field splitting, so that spin-up \( t_{2g} \) and \( e_g \) states are filled and the spin-down ones are empty. As a consequence, the exchange splitting does not change the ratio of the two peaks and the intensity ratio \( t_{2g}/e_g \) should be \( \frac{1}{2} \cdot 2 = 0.38 \) when the different hybridization is taken into account. This is far lower than the values measured (1.0 and 1.6).

**F. Possible reasons for the discrepancies**

In the solid, bond formation leads to broadening of the \( t_{2g} \) and \( e_g \) levels. It is probable that the \( t_{2g} \) and \( e_g \) descriptions are only approximately applicable to the two peaks observed and to some extent \( t_{2g} \) and \( e_g \) character is spread throughout the whole region of the unoccupied 3d levels. This will modify the spectra directly. In addition, it opens the possibility for the core-hole potential to shift weight towards the threshold. We have argued earlier that the influence of the core hole on the oxygen 1s site is small because the unoccupied states have principally metal 3d character. However, this does not mean it can be ignored completely in the context of intensity distributions within the rather narrow, empty 3d region. There may be other reasons for the anomalous intensity ratios we find, but we feel that these two effects of band formation cannot be dismissed without further quantitative investigation.

A further reason of discrepancies might be found in the nonstoichiometry of some samples; defects distort the local symmetry and lead to some variation in the interatomic distances. This results in a variation in the amount of hybridization, which in principle can influence the \( t_{2g} \) versus \( e_g \) intensity distribution and also the ligand-field splitting. We note that although computed charges of the vanadium 1s XAS spectra from VO\(_{0.8}\) to VO\(_{1.25}\) are quite large, published vanadium 1s spectra show a smaller sensitivity, which, if reproduced at the oxygen 1s edges, would not be large enough to explain the discrepancies we observe. Although we have not considered defects in detail here, we have measured NiO in its black (defect-rich) and green form. Their oxygen 1s XAS spectra were identical, which suggests that defects are not too critical for the shape of the spectra. A study of Li-doped NiO (or Ni\(_{1-x}\)Li\(_x\)O) which results in oxygen 2p holes, revealed that besides the extra peak at the edge (2p hole states) the rest of the spectrum did not change much, except for an increasing width of the peaks. This may not be true for highly defective oxides, like VO and TiO, and the question of the influence of defects deserves much more detailed study. However, the results discussed in this paragraph suggest that defects cannot explain the discrepancies we discuss.

**V. CONCLUDING REMARKS**

All oxygen 1s absorption edges of the transition-metal oxides can be divided into two regions. In the first, near threshold, the oxygen 2p character is hybridized with the sharp structured transition-metal 3d band. In the second region, O 2p character is hybridized with the weakly structured 4sp band. The integrated intensity of the 4sp region is at least equal to the 3d-bond region, which indicates that the metal 4sp states are important for the covalency of the transition-metal oxides. The metal 4sp hybridization gives a more or less constant bonding effect above which the metal 3d hybridization accounts for the specific, material-dependent, effects.

The 3d band consists of two peaks, which we believe are mainly related to, respectively, \( t_{2g} \) and \( e_g \) symmetry, despite the observation of anomalous intensity ratios. For all oxides considered, the ligand-field-splitting parameter, from optical spectroscopy, is well reproduced by the separation of the first two sharp XAS peaks. For Cr\(_2\)O\(_3\) and Mn\(_2\)O\(_3\) the description of the combined effect of ligand-field and exchange splitting leads to the conclusion that the first peak is an "accidental" superposition of \( t_{2g} \) spin-down and \( e_g \) spin-up states, while the second peak relates to the remaining \( e_g \) spin-down states.

The intensities of \( t_{2g} \) and \( e_g \) do not conform with the rule that \( e_g \) hybridization is twice as big at \( t_{2g} \) hybridization. Across the series the intensity of the \( t_{2g} \) peak is underestimated. The reason is not clear to us, but we believe that band formation in the solid, with all its consequences, may explain at least some of the discrepancies.

Our analysis showed that an important factor determining the shape and magnitude of the 3d region in the oxygen 1s XAS spectra of the 3d-transition-metal oxides is the presence of a filled \( e_g \) orbital in the ground state. This criterion splits the 3d-transition-metal oxides into two main groups: the early- (or light) 3d-transition-metal oxides with zero to three \( d \) electrons, and the late- (or heavy) 3d-transition-metal oxides with five or more \( d \) electrons, which are more localized.

**ACKNOWLEDGMENTS**

We thank S. Hüfner for constructive discussions, W. Braun for his efforts in coordinating our experiments, and B. E. Watts for provision of a single crystal of CuO. We are grateful to the staff of the Berliner Elektronen Speicherring-Gesellschaft für Synchrotronstrahlung.
(BESSY) for their support. This work was supported, in part, by the Dutch Foundation for Chemical Research [Stichting Scheikundig Onderzoek Nederland (SON)] with financial assistance of the Netherlands Organization for Scientific Research [Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)] and by the Committee for the European Development of Science and Technology (CODEST) program.


10Examples of high-resolution monochromators for the oxygen 1s edge (500 eV) are the SX700 at BESSY, Berlin, H. Petersen, Nucl. Instrum. Methods A 246, 260 (1986); the 10-m grazing-incidence monochromator at the Photon Factory, H. Maezawa, S. Nakai, S. Mitani, A. Mikuni, T. Namioka, and T. Sasaki, Nucl. Instrum. Methods A 246, 310 (1986); and the Dragon monochromator at Brookhaven National Laboratory, C.T. Chen, Nucl. Instrum. Methods A 256, 595 (1987). The pace of development in this area is so high that within the last year 500 meV resolution can be significantly bettered in some instruments.


12For example, L. Hedin, Phys. Rev. 139, A796 (1965).

13We know of only one oxide band-structure calculation (for CuO), whose basis set includes also the metal 4s and 4p and the oxygen 3s and 3p states and thus is more appropriate for a comparison with oxygen 1s XAS. A detailed comparison for CuO is given by M. Grioni, M. T. Czyzyk, F. M. F. de Groot, J. C. Fuggle, and B. E. Watts, Phys. Rev. B 39, 4886 (1989); the theoretical and mathematical details concerning this extended basis set are discussed by M. T. Czyzyk and R. A. de Groot (unpublished).


30This assignment does agree with, e.g., P. R. Sarode, J. Phys. F 17, 1605 (1987).

31K. Fajans and G. Joos, Z. Phys. 23, 1 (1923); K. Fajans, Naturwissenschaften 11, 165 (1923); Z. Kristallogr. 61, 18 (1924).


38 W. Harrison, in Electronic Structure and Properties of Solids (Freeman, San Francisco, 1980).


41 This is reflected in a band-structure calculation of TiO₂, as given by S. Munnix and M. Schmeits, Phys. Rev. B 30, 2202 (1984).

