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X-ray absorption of transition metal oxides: an overview of the theoretical approaches[1]

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Abstract

A short overview is given of the different approaches to interpreting X-ray absorption spectroscopy (XAS), and particularly their relation to electronic structure models. The electronic structure models which incorporate many-electron effects, such as GW calculations, the Hubbard model and self-interaction corrected local density approximation (LDA) calculations, are outlined. Special attention is given to the use of Hubbard model for core level spectroscopies. Within this background two extreme models for interpreting X-ray absorption spectra are discussed in detail: the ligand field multiplet model to interpret metal 2p-XAS spectra and LDA calculations to interpret oxygen 1s-XAS spectra. Finally the open problem of possible final state effects on model hamiltonians is outlined.

Introduction

In this paper a short review is given of the models and ideas currently in use for the interpretation of X-ray absorption spectroscopy (XAS) of transition metal oxides. As such this paper is a recollection of what I have learned during my study in John Fuggle's group.

A main goal of spectroscopic studies such as X-ray absorption and photoemission is to establish an accurate picture of the electronic structure of solids. A problem is that the electronic structure of transition metal oxides is not accurately known. Great efforts are made to improve this description and the role of spectroscopies like X-ray absorption is to pinpoint problems in the models presently at use. Conversely, the models used to interpret X-ray absorption must be adapted to changes in the electronic structure models.

The next section gives a short overview of the models used for the description of the electronic structure of solids. The third section describes core level excitations. The fourth section focuses on the Hubbard model

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[1] Dedicated to the memory John C. Fuggle.

description of core level spectroscopies. The fifth section deals with the ligand field multiplet model used for the analysis of 2p-XAS. The sixth section describes the analysis of oxygen 1s-XAS in terms of local density approximation (LDA) calculations. The final section briefly discusses the possible final state effects of parameters in model hamiltonians.

Models used to describe electronic structure

Single particle models

To describe the ground state of solids a dominating role is played by models which use a single particle description [1]. Since the establishment of the density functional theorem stating that the ground state energy can be expressed as a functional of the electron density [2] and the practical implementation of this theorem in the LDA [3], solid state calculations based on this formalism have become important. This is true not only for determining the total energy but also for obtaining a picture of the electronic structure in terms of the density of states, which in turn is used to analyze spectra.

Within the single particle description the usual picture used to visualize the electronic structure of a transition metal oxide is to describe the chemical bonding mainly as a bonding between the metal 4sp states and the oxygen 2p states, forming a filled bonding combination (the valence band) usually denoted as the oxygen 2p band, and empty antibonding combinations. The 3d states couple mainly with the oxygen 2p states, which causes then to be anti bonding in nature. Additionally, this bonding, taking place in a (distorted) cubic crystalline surrounding of oxygen atoms, causes the 3d states to be split into the t_{2g} and e_g manifolds. This qualitative description of the electronic structure of transition metal oxides can be worked out quantitatively within the LDA. The only approximation *within* LDA calculations of solids is the limitation in the number (and nature (see, for example, ref. 4)) of basis functions [5]. Spin polarization and spin–orbit coupling are often neglected in actual calculations and the necessity for including them depends on the goals of the calculation. (Here we also use the term LDA for spin-polarized relativistic versions, sometimes denoted as LSDA.)

Many-electron effects

The question of what is missing in single particle models can be answered simply by many-electron effects. This, however, does not solve the problem because it is impossible to consider all many-electron effects. Thus, in order to continue it is necessary to make a particular choice for the kind of many-electron effects which are important. This choice depends on the particular experiments one wishes to describe.

GW calculations

A well defined model for describing electronic excitations is the so-called GW approach [6] in which the screened Coulomb interaction W is used to calculate the excitation energies. The calculation requires a non-local energy-dependent so-called self-energy operator. A GW calculation gives the density of (quasi-particle) states for the occupied states of the $N-1$ system and the empty states of the $N+1$ system. Hence it gives a direct description of (inverse) photoemission spectra. This is in contrast to LDA calculations, which can be considered as GW calculations with a local energy independent self-energy operator, thereby yielding an "N-particle density of states". The actual calculation of excitation energies with GW is a large task, especially for transition metals because of the narrow d bands, and to my knowledge only for nickel has a GW calculation been performed [7]. For transition metal oxides no GW calculation has been published to date [8].

The Hubbard model

A crucial phenomenon in transition metal oxides is the fact that it costs energy to transfer an electron from one metal ion to another, because of strong two-electron integrals $\langle 3d,3d|1/r|3d,3d\rangle$, comprising the Coulomb repulsion energy U_{dd}. In LDA and GW calculations this effect is not incorporated correctly and each transition metal contains the same number of (completely delocalized) electrons. In practice, to put a number to the occupation one usually assigns all electrons within a particular radius to that atomic site. The fact that U_{dd} is not small means that it costs energy to vary the occupation number of the metal sites and in the extreme limit of infinite U_{dd} each metal site contains an integral number of localized 3d electrons. The consequences of U_{dd} have been realized since the 1960s and models have been built focusing on a correct description of the Coulomb repulsion, at the expense of less complete descriptions of other components [9]. The model hamiltonians built from this approach usually consist only of the 3d states and the oxygen 2p states. The original Hubbard cluster model comprises the energy positions ε_d and ε_p, Coulomb repulsion U_{dd} and hopping matrixes t_{pd} and t_{pp} [10]. The model can be modified to an impurity-model by rendering the 2p-states into a band [11]. The Hubbard model is often extended by including the Coulomb repulsion of the 2p states (U_{pp}, U_{pd}): the three-band model [12]. Hubbard models are crucial for a sensible description of photoemission, inverse photoemission and core level X-ray photoemission spectra of transition metal compounds [13]. The model parameters can be calculated with ab initio methods using constrained LDA calculations [14]. A further step is to include U_{dd} into the LDA calculations: the so-called LDA + U calculations. Recently, LDA + U calculations have been performed for transition metal oxides by Anisimov et al. [15].

Self-interaction correction (SIC)

An alternative approach to introduce the localization effect due to the two-electron integrals is to introduce a so-called SIC. In LDA calculations non-existing self-interactions are included in the electrostatic (Hartree) term and also in the exchange-correlation term. The effects are opposite and tend to cancel out, and in fact for the case of an infinitely extended solution they do cancel out. However, in a strongly correlated material the wavefunctions are not infinitely extended and a correction must be added to the hamiltonian removing the effects of self-interaction: the SIC [16–20]. In order to have the possibility to find a localized solution of the LDA + SIC calculations, a symmetry-breaking term is introduced. It is tested self-consistently if a localized solution is favored over delocalization. For example, for the 3d monoxides localized solutions are found for CrO to CuO in agreement with experiment [18, 20]. In principle, the result of a LDA + SIC calculation is "single particle"-like. As for normal LDA, the eigenvalues can be related to excitation energies (although again there is no formal justification). A remarkable result is that, for example, the d^7 satellite in NiO is correctly reproduced in LDA + SIC [21].

Multiplet effects (orbital polarization)

Apart from the direct Coulomb repulsion energy, the evaluation of the two-electron integrals $\langle 3d,3d|1/r|3d,3d\rangle$ comprises higher-order interactions, denoted by the Slater integrals F^2 and F^4 [22]. These higher-order effects are at the origin of the so-called Hund's rules, which determine the non-spherical symmetry of the states. They have been incorporated into LDA calculations under the heading of orbital polarization [23,24] and naturally they are at the core of atomic multiplet theory [22].

Core level excitations

Core level X-ray photoemission

In core level X-ray photoemission spectroscopy (XPS) the electron is excited to an energy high above the Fermi level and it can be considered as a free electron. The shape of the XPS spectrum is determined by the reaction of the system on the core hole. If no reaction takes place the outgoing electron measures the binding energy of the core level. However, the system reacts on the core hole by relaxation processes. For example for

2p XPS an important effect is the two-electron integral $\langle 2p,3d|1/r|2p,3d\rangle$, giving rise to a core hole potential U_{cd}. (The core hole spin–orbit coupling is important too and gives rise to the $2p_{3/2}$ and $2p_{1/2}$ edges, but this is not considered here.)

Within the Hubbard model, the interaction of a 2p core hole will stabilize states which contain more 3d electrons. For the late 3d transition metal compounds the energy position of the ligand band is only slightly above the 3d states and the energy difference will be smaller than the core hole potential ($\varepsilon_d - \varepsilon_p < U_{cd}$). This implicates that the ordering of states in the final state is modified: the charge transfer effect. This has been shown in detail for the nickel halides [25]. The importance for electronic structure description is that in the analysis of the 2p XPS spectra, (some) parameters which are used in the Hubbard model can be determined more accurately than in the corresponding valence spectra.

A problem in this analysis is that it is not a priori true that the parameters are equal in the initial and final state. In the analysis the same set of parameters is usually used with only the addition of U_{cd} in the final state. This problem is returned to in the final section (Final state effects on model parameters).

The higher-order terms of the core hole interaction with the 3d band are also important, and in fact in the final state these effects are more important. The two electron integrals $\langle 2p,3d|1/r|2p,3d\rangle$ and $\langle 2p,3d|1/r|3d,2p\rangle$ contain the higher-order terms F^2, G^1 and G^3. They have large values and give rise to a series of final states with different symmetries and energies: the final state multiplet. In general these effects are denoted as multiplet effects. For photoemission the final state is a free electron, hence the dipole selection rule is relaxed and all final state symmetries are allowed. Actual calculations including both the charge transfer effects and multiplet effects have been published by Okada et al. [26–29]. In conclusion, one can state that the importance of the 2p–3d integrals *localizes* the problem and necessitates the use of both the Hubbard model and multiplet effects. These effects are particularly large for 2p and 3p spectra of transition metals and 3d and 4d spectra of rare earths and actinides.

X-ray absorption

In XAS the energy of the X-ray is varied through a core level and an electron is excited to a state just above the Fermi level. If no reaction with the core hole takes place, the shape of the XAS spectrum will reflect the density of empty states (times transition strengths). Because in X-ray absorption the excited electron is not free, the dipole transition poses strong selection rules to the final state. This gives X-ray absorption its site and symmetry selective properties, and for example oxygen 1s X-ray absorption will reflect the oxygen p-projected density of states.

However, the core hole cannot be neglected and for 2p X-ray absorption the 2p core hole will again couple strongly to the 3d states, both via its potential and via its higher-order (and exchange) terms; for their analysis the charge transfer plus multiplet models must be used. There is an important difference between 2p XPS and 2p XAS with regard to the relative importance of charge transfer versus multiplet effects; one can roughly state that 2p XPS is dominated by charge transfer whereas 2p XAS is dominated by multiplets. This is discussed in detail in the next section (The Hubbard model for core level spectroscopies).

For 1s X-ray absorption the situation is less clear. The higher-order terms of the two-electron integrals with the core hole are negligible. The final state contains $N+1$ electrons in the valence band and if one neglects the origin of the extra electron a direct analogy with inverse photoemission spectroscopy (IPS) is evident. This suggests comparing the spectral shape with the Hubbard model calculations used for IPS [30]. If one also neglects the valence state two-electron integrals a GW calculation would yield the correct result.

However, there is a difference with IPS, i.e. the existence of a core hole. The actual final state is $\underline{c}N+1$, which still is an N-electron system. The effect of the core hole on X-ray absorption has been much studied [31]. Von Barth and Grossmann postulated a final state rule, which states that the X-ray absorption spectral shape is given by the final state density of states (DOS) [32]. This final state DOS can be calculated in an impurity calculation. To reshape this into a band structure calculation a supercell can be set up, with dimensions large enough to effectively eliminate hole–hole interactions [33]. Another approach is to use a ground state calculation and to impose a core hole potential on the DOS [34]. If the core hole potential is ineffective with regard to modifying the spectral shape, a LDA ground state calculation will give a similar result. In the sixth section (Oxygen 1s XAS interpreted with LDA calculations) this is discussed further and some examples are given.

The Hubbard model for core level spectroscopies

In the Hubbard model the 3d states are considered localized. They are positioned at an energy ε_d with a Coulomb repulsion energy U_{dd}. They interact with ligand 2p states (or bands) at energy position ε_p; the hopping matrixes are t_{pd} (and t_{pp}). The starting point is a specific 3d configuration $3d^N$. If the hopping of this localized state with the filled 2p band is considered, this gives rise to $3d^{N+1}\underline{L}$ configurations at an energy $\varepsilon_p - \varepsilon_d$, which is also denoted as Δ: the charge transfer energy. In the final state of both

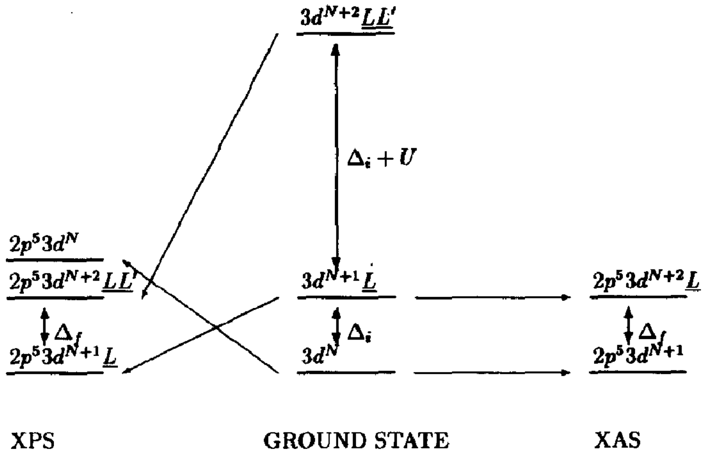


Fig. 1. 2p XPS and 2p XAS in the charge transfer model, neglecting the effects of hybridization. The configurations with lowest energy in the initial and the two final states are set to zero. $\Delta_f = \Delta_i + U_{dd} - U_{\underline{c}d}$. The arrows indicate the transitions in both 2p XPS and 2p XAS.

2p XPS and 2p XAS a core hole is present which couples strongly to the 3d states via $U_{\underline{c}d}$, which pulls down states with extra 3d electrons.

These four parameters Δ, t_{pd}, U_{dd} and $U_{\underline{c}d}$ basically determine the shape of the 2p XPS and 2p XAS spectra (neglecting multiplet effects). This is visualized for a typical charge transfer insulator (Δ = 3, U_{dd} = 7 eV) in Fig. 1, in which the ionic configurations are given and the effects of hybridization are not included. The arrows indicate the transitions in both XPS and XAS. In XPS the ordering of the final states is changed dramatically because of the effect of $U_{\underline{c}d}$. In XAS the ordering of states in the final state does not change because the 2p electron is excited directly into a 3d state, which causes the counteracting effects of U_{dd} and $U_{\underline{c}d}$. In general $U_{\underline{c}d}$ is slightly larger than U_{dd}. However, for simplicity they are taken to be equal, with the consequence that $\Delta_f = \Delta_i + U_{dd} - U_{\underline{c}d} = \Delta_i$.

In Fig. 2 the effects of hybridization are included for 2p XAS. The ground state is formed from a combination of $3d^N$ and $3d^{N+1}\underline{L}$. The two configurations in the final state form a bonding and antibonding combination. With the restriction that $U_{\underline{c}d} \approx U_{dd}$ all intensity goes to the bonding combination of the two final state configurations and no satellite is present [35].

In the case of 2p XPS the situation is rather different. In general there are three low-lying states in the final state and their ordering has been changed with respect to the ground state. Under complete neglect of hybridization only the $2p^5 3d^N$ final state can be reached. If hybridization is turned on, the two lower states gain in intensity, partly due to ground state hybridization but mainly due to final state hybridization and additionally due to the interference terms. This has been shown nicely for the nickel halides, for which all model parameters can be chosen equal with only the charge

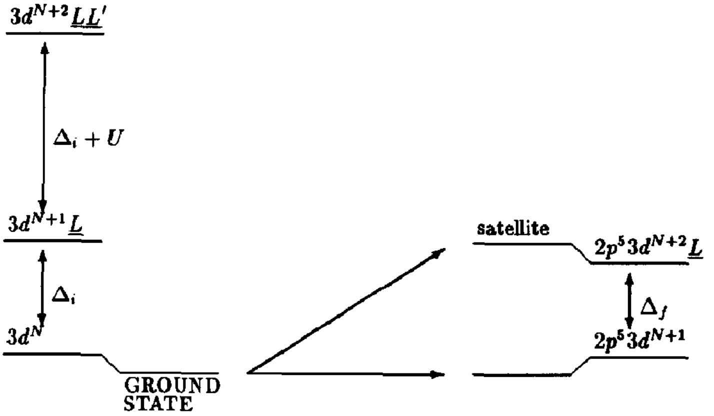


Fig. 2. The effects of hybridization on 2p XAS. If $\Delta_f = \Delta_i$ (and $t_f = t_i$) only the transitions to the lowest mixed configuration in the final state occur (see text).

transfer Δ decreasing from fluoride to iodide, giving rise to a large variety in spectral shapes.

From this discussion it can be concluded that the 2p XPS spectrum will contain large charge transfer satellites, whereas the 2p XAS spectrum in principle only shows a single peak (with its multiplet splittings). This difference between 2p XPS and 2p XAS can be summarized as follows: XPS is sensitive to the charge transfer effects, or in other words to the electronic configuration of the ground state; XAS is sensitive to the symmetry of the ground state with its characteristic multiplet.

Interplay between charge transfer and multiplet effects

We assume that in a final state of 2p XAS the multiplet lines are spread out over an energy range of several eV (for details of multiplet calculations see the next section (The ligand field multiplet model for 2p XAS)). This spread implies that the energy difference of these different states with the $2p^53d^{N+2}\underline{L}$-band varies considerably. In Fig. 3 a situation is sketched in which the multiplet splittings $\delta/2$ are less than the charge transfer energy Δ. If hybridization is turned on the energy-gain of the lowest multiplet state (Γ_1) will be less than the energy-gain of the highest multiplet state, because the effective energy difference with the band is much smaller in the latter case. In the case of a multiplet with 100 lines instead of two this principle remains valid. The consequence is that the multiplet structure is "compressed" with respect to the atomic multiplet. If the spread of multiplet states is larger than the charge transfer energy, some of the multiplet states will be located within and above the band and the effects of charge transfer will be more complex.

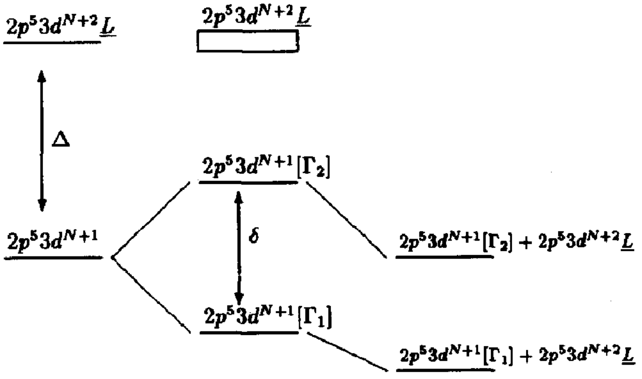


Fig. 3. The interplay of multiplet and charge transfer effects. If, as indicated, $\Delta > \delta/2$, the net effect is a compression of the multiplet structure. If $\Delta < \delta/2$ the effects of charge transfer will be more complicated.

The ligand field multiplet model for 2p XAS

As previously discussed, charge transfer effects are less effective in 2p X-ray absorption and in this section we neglect them altogether. What remains is a description of localized 3d states.

The procedure is as follows. In the first step the states of a transition metal atom (or ion) are calculated for a particular $3d^N$ configuration describing the ground state. The atomic hamiltonian is solved by a Hartree-plus-statistical-exchange (HX) method, which is corrected for correlation effects [22]. The same procedure is used for the $2p^5 3d^{N+1}$ final state. This calculational method is to be considered as a single-particle method because it describes the ground state with a single Slater determinant, though an important difference from the LDA is the correct inclusion of the two-electron integrals in the HX method. This method has been developed for atomic spectroscopy and detailed comparison with experiments have revealed that the quantitative agreement is not good. To improve the description many-electron effects have been included by means of configuration interaction (CI) procedures, but the problem is still not solved satisfactorily [36]. It has been found that the disagreement with experiment is largely solved by an empirical correction to the Slater integrals. Reducing them to about 80% of their HX values results in a detailed comparison with experiment. Theoretical studies have indicated that the excited configurations have an equivalent dependence on the spin and angular momenta as the ground state, but with the opposite sign [37]. This implies that including these excited configurations in CI calculations effectively reduces the Slater integrals.

From atoms to solids

If one transfers this atomic method to the solid state, the first question to ask is whether it is possible at all to describe a 3d state in a solid quasi-atomic. The discussion of the Hubbard model has learned that because of the counteracting efforts of U_{dd} and U_{cd} this is indeed the case for X-ray absorption. However, there remains the problem of how to accommodate the atomic states in the solid state environment. Particular questions are (1) how to deal with the different local symmetry and (2) how to incorporate the different more itinerant electronic features of the solid state, such as the electron density of the s and p states. The inclusion of the local symmetry has been the subject of many studies under the heading of ligand field theory [38]. This has been used particularly to describe the optical absorption spectra of transition metal ions. For core level spectroscopies ligand field theory was developed in the 1970s [39]. A first general program, including the effects of 3d spin–orbit coupling and usable for all point group symmetries, has been developed by Thole et al. [40].

The itinerant effects of the solid have been described under the heading nephelauxatic effect [41] with the analogy to expanding clouds, hence smaller on-site overlap. This means in practice that the Slater integrals are reduced from their atomic value (which is 80% of HX), with the effect that the spectrum appears compressed. In the Hubbard model description the main effect of the solid are the charge transfer excitations, which will again effectively compress the multiplet splitting as described in the previous section (The Hubbard model for core level spectroscopies).

Symmetry effects in solids

In the following we focus on the symmetry effects and we neglect the charge transfer effects. The dominant symmetry effect in solids is the cubic crystal field, which can be described by a single operator which is added to the hamiltonian. The strength of this operator is usually denoted as the crystal field splitting ($10Dq$). The procedure is as follows. The atomic $3d^N$ and $2p^5 3d^{N+1}$ configurations are recalculated with the inclusion of $10Dq$ as a free parameter. The X-ray absorption spectrum is given by the transition strength of the lowest state of the $3d^N$ multiplet to all $2p^5 3d^{N+1}$ final states. If in the ground state two (or more) states have an energy separation of the order of the measurement temperature, a Boltzman distribution is used. Figure 4 shows a series of calculations for the transition $3d^0 \rightarrow 2p^5 3d^1$ [42]. Figure 5 gives a comparison with experiment for $SrTiO_3$, for which titanium is described as Ti^{4+}. It can be seen that a quasi-atomic calculation gives a quantitatively good description for this system. This raises the question of how it is possible that titanium can be described as tetravalent, when, for

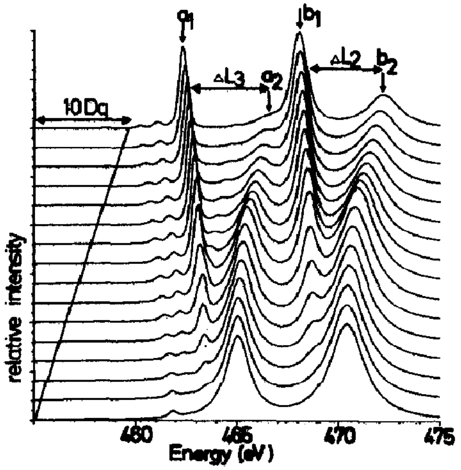


Fig. 4. Ligand field multiplet calculations for the $3d^0 \rightarrow 2p^5 3d^1$ transition in tetravalent titanium. The size of the cubic crystal field splitting is increased from zero (bottom) to 4.5 eV (top).

example, band structure results show that the actual charge transfer from titanium to oxygen is small and certainly not four electrons [43]. The answer is that what matters is the symmetry of the ground state and because the 3d band is completely empty this is clearly ^1S for titanium in $SrTiO_3$. The comparison confirms that charge transfer effects are not effective.

The sensitivity of 2p X-ray absorption to the ground state symmetry is in fact its great merit because it can be used to determine the symmetry of

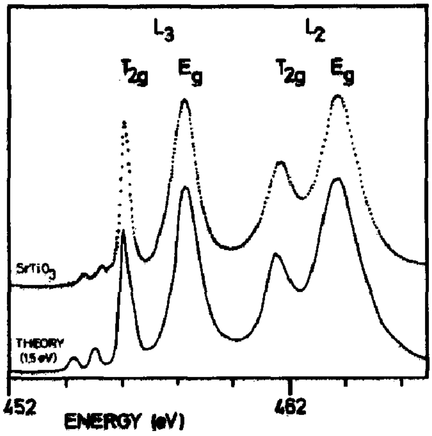


Fig. 5. Titanium 2p X-ray absorption spectrum of $SrTiO_3$ compared with a crystal field multiplet calculation.

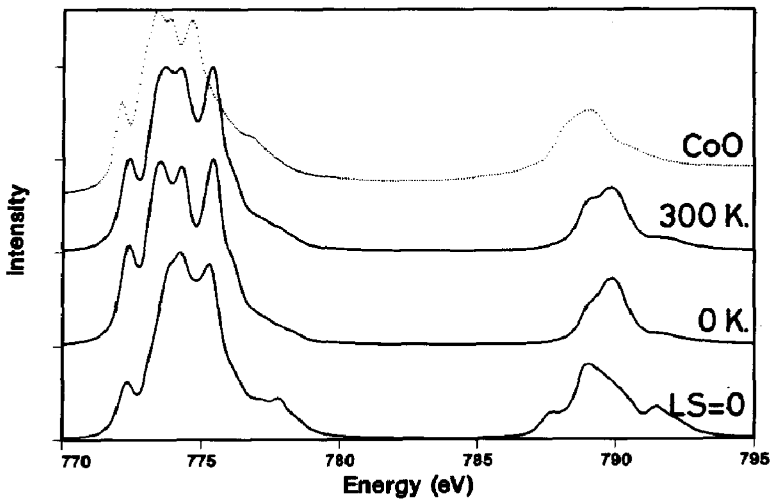


Fig. 6. The cobalt 2p X-ray absorption spectrum of CoO (top), compared with ligand field multiplet calculations of the $3d^7[^4T_1] \rightarrow 2p^5 3d^8$ transition. In the bottom spectrum 3d spin–orbit coupling is neglected. The two middle spectra are calculated with the atomic 3d spin–orbit coupling for respectively 0 and 300 K.

transition metal ions in unknown systems and its obvious difference with optical absorption is its element specificity.

For a transition metal ion in a (distorted) octahedral crystal field there are the following effects on the symmetry.

(1) The strength of the cubic crystal field determines the high-spin or low-spin nature of the ground state for an ionic configuration with from four to seven 3d electrons [38]. The spectral shape changes at a high-spin low-spin transition because the final state multiplet is different.

(2) The 3d spin–orbit coupling is of the order of 50–100 meV for 3d transition metal ions. It will cause low-energy splittings of this order of magnitude for all ground states with a partly filled t_{2g} band, or in other words with T_1 or T_2 symmetry. For states with an E symmetry ground state the effect is an order of magnitude smaller because 3d spin–orbit coupling affects e_g orbitals only in second order [38]. A particularly sensitive system is high-spin $3d^7$ and Fig. 6 demonstrates the effect for CoO [44,45].

(3) In general, the spectral shape will not be very sensitive to distortions from cubic symmetry. Only in cases with large distortions, such as Jahn–Teller distorted partly filled e_g bands are effects likely to be observable in the overall spectral shape. (For polarization dependence see the next section.)

(4) Magnetic effects are of the order of a few meV and will not be detectable in the overall spectral shape of X-ray absorption.

This implies that from a 2p X-ray absorption spectrum one can accurately determine the valency, its high-spin or low-spin nature, including the size of the cubic crystal field, and also the effect of 3d spin–orbit coupling. To determine lower symmetries and magnetic effects one has to make use of the polarization dependence of the spectral shape.

Polarization dependence

In the multiplet model the transition strength is given by

$$\langle \phi(JM) | r_q | \phi(J'M') \rangle = (-1)^{J-M} \begin{pmatrix} J & 1 & J' \\ -M & q & M' \end{pmatrix} \langle \phi(J) \| r_q \| \phi(J') \rangle \quad (1)$$

The intensity of the peaks is given by the addition of the three polarizations of the X-ray ($q = 1, 0, -1$) times the reduced matrix element (squared). Polarization dependence is achieved as follows. Synchrotron radiation is linearly polarized in the plane of the electrons and out-of-plane the radiation is partly circularly polarized [46]. Linear dichroism spectra are measured by turning the sample, which modifies the polarization from $q = +1, -1$ at normal incidence to $q = 0$ at grazing incidence. Circular dichroism spectra are measured by using only light from either above or below the plane. The result must be corrected for the actual degree of circular polarization.

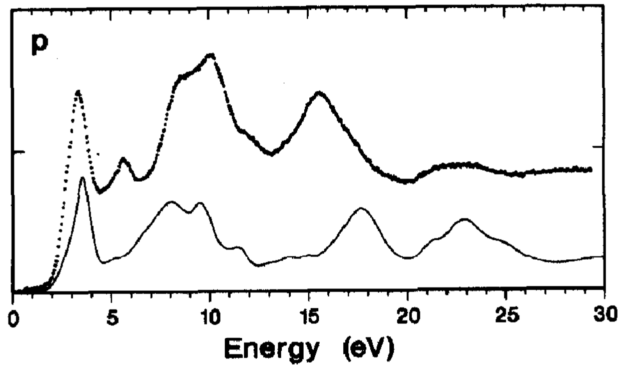
With linear dichroism the asymmetry of the electronic states around a transition metal atom is measured, for example the asymmetry of states in layer compounds [47], or at surfaces [48]. With circular dichroism the difference between $q = 1$ and $q = -1$ transitions is measured, in other words the (ferro) magnetic ordering [49]. A magnetic ordering, either ferromagnetic or antiferromagnetic will also give rise to a linear dichroism effect (with regard to the magnetization axes), additional to any asymmetric crystalline and surface effects [50]. From the MCD spectrum one can determine the magnetic moment [51] and it has also been shown that the (normalized) integrated MCD intensity is a measure of the orbital polarization [52]. Experimentally quantitative MCD measurements are more demanding with regard to the sample cleanliness, the degree of magnetization and the degree of polarization.

Oxygen 1s XAS interpreted with LDA calculations

As has been discussed in the third section (Core level excitations) for oxygen 1s X-ray absorption of transition metal oxides the following effects/interactions are important for the spectral shape:

(1) hybridization effects as described in a single particle calculation;
(2) addition of an electron in the conduction band;
(3) two-electron interactions within the 3d band;
(4) the core hole potential.

(a) Oxygen k edge of SrTiO$_3$



(b) Oxygen k-edge of TiO$_2$ RUTILE

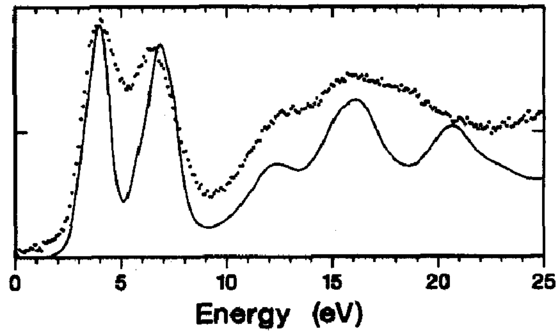


Fig. 7. Comparison of the oxygen 1s X-ray absorption spectra with the oxygen p-projected DOS of (a) SrTiO$_3$ and (b) TiO$_2$.

The following models can be used (the interactions which are included in the various models are given):

LDA calculation, (1);

GW calculation, (1) + (2);

Hubbard model, (1) in cluster approximation, (2) + (3); ref. 53, also (4);

Final state LDA calculation, (1) + (2) + (4).

First to be considered are oxides with an empty 3d band, which removes effect (3), and hence removes the need for the Hubbard model. For this class of materials final state DOS calculations should give the correct result, but ground state LDA calculations are used first. Figure 7 gives a comparison of the oxygen p-projected DOS with the oxygen 1s X-ray absorption spectrum of SrTiO$_3$ and TiO$_2$ (rutile) [43]. The agreement for TiO$_2$ is good and all peaks are reproduced at approximately the correct energy. This justifies the conclusion that for TiO$_2$ the effect of the core hole potential is too small to modify the spectral shape significantly, which makes ground state LDA calculations suitable. For SrTiO$_3$ the agreement is less good and in particular the e_g peak in the experiment is not reproduced in the calculations. The e_g peak is positioned just at the bottom edge of the e_g band in the calculations (see ref. 43 for details). In $SrTiO_3$ the e_g band is wider (and flat-shaped) than in TiO_2 because of the different crystal structures. Additionally, in $SrTiO_3$ the bandwidth is determined solely by dispersion, whereas in TiO_2 most of the width originates from distortions of the octahedra. Hence, a core hole potential will act differently on both systems. For TiO_2 the effect of the core hole potential will be smaller because it cannot counteract broadening from the distortions. In fact in this case the e_g band is not a single band but must be considered as two overlapping bands, which means that the core hole potential affects these bands "independently", i.e. it cannot transfer weight from one band to the other. Apart from this, the particular shape of the band also makes $SrTiO_3$ more susceptible to effects of the core hole potential.

The overall conclusion is that for transition metal oxides with an empty 3d band the oxygen p-projected density of states of a LDA calculation gives a good simulation of the spectral shape. The effectiveness of the core hole potential largely depends on details in the crystal structure.

For transition metal oxides with a partly filled 3d band the Hubbard model description becomes crucial for the electronic structure. However, for the empty states only the 3d band related states are likely to be affected by two-electron integral effects. The other states are so delocalized that they will still be equivalent to the DOS as calculated from the LDA. Cluster calculations with the Hubbard model including multiplet effects, originally developed for IPS, have been used to simulate the oxygen 1s X-ray absorption spectra of CoO and NiO [30]. As yet, the results are not convincing and in particular there are problems with regard to the intensity ratio of the t_{2g} and e_g peaks. There are also questions with regard to the usability of the model because it changes the number of electrons and thereby neglects the core hole and leaves uncertainties with regard to the parameters in the final state. Because of these uncertainties it is not yet possible to give a detailed answer to the question of the importance of two-electron integrals in oxygen 1s X ray absorption.

From LDA + U and LDA + SIC band structure calculations it has been found that the empty states are not modified from normal LDA calculations, in considerable contrast to the occupied states [54]. In these calculations for the empty density of states only a rigid shift is observed. Thus, as far as the spectral shape is concerned ground state LDA calculations can also be compared with oxygen 1s X-ray absorption spectra. Results have been published for CuO [55] and $LiCoO_2$ [56] and in both cases good agreement has been found. However, these are rather special cases: CuO because it is a $3d^9$ system and there are no multiplet effects in the final state; $LiCoO_2$ because it is a low-spin $3d^6$ system with all t_{2g} states filled and all e_g empty.

The (spin-polarized) LDA calculations for MnO and CoO as performed by Terakura and co-workers [57] show for the empty spin-down t_{2g} and e_g bands split by the cubic crystal field, in close agreement with the oxygen 1s X-ray absorption results [58,59]. Thus, the observations made so far do not pinpoint clear differences between LDA calculations and oxygen 1s X-ray absorption, despite the fact that there must be effects from the 3d–3d two-electron integrals.

Final state effects on model parameters

This section deals with an important issue for the model hamiltonian description of core level spectroscopies: the final state effects on the model parameters used. In many papers this question is not touched and it is tacitly assumed that identical parameters can be used both in the final state and in the initial state. This is, however, far from evident. The interesting model parameters are the Coulomb repulsion U_{dd}, the (symmetry dependent) hopping terms t_{pd}, and the cubic crystal field splitting $10Dq$. Normally it is assumed that the final state is described by adding U_{cd}, affecting the energy positions of the states.

The hopping parameter t_{pd} is defined as the matrix element between the localized states and the band. In the original definition this was denoted as $b_{ij} = \langle\phi_{\mathrm{d}}(r)|V|\phi_L(r - R)\rangle$, with ϕ_{d} as the localized states [60]. On theoretical grounds Zaanen [11] estimated that for the nickel halides the hopping should increase in the final state of 2p XPS, owing to the presence of the core hole, which gives an extra term in the matrix element. Gunnarsson et al. [61] analyzed the final state hopping in detail. They pointed out two counteracting effects: (1) the extra term in the matrix element; (2) the fact that ϕ_{d} tends to localize because of the core hole. For Mn in CdTe the finding is that if a core hole is included the hopping is reduced by about 20%. In other words the localization effect seems to dominate the extra hopping term.

Apart from differences between initial state and final state there can also be differences between different core level excitations, for example 2p XPS and 2p XAS, particularly because the screening processes will be different. If the hopping in the final state is indeed different from the ground state this will affect the spectral shape. Another consequence is that if a (single) value for the hopping is determined empirically from core level spectroscopy it will be the final state value (or a kind of mean value).

Apart from the theoretical findings concerning the final state effect on the hopping, there are some empirical hints. In the empirical determinations of the hopping a variation is found between different studies and, for example, for CoO a larger value for the hopping is determined from 2p XPS [62] than from PES/IPES [30]. A similar variation has been found for cerium intermetallics [63]. Further experimental evidence for final state effects on model parameters concerns the value of the cubic crystal field splitting 10*Dq*. In a 2p XAS study of a series of manganese compounds it has been found that the final state crystal field splitting is decreased to about 75% of the initial state values (determined by optical spectroscopy). A similar result has been found for titanium oxides [43]. The value for 10*Dq* is closely related to the hopping. Usually the value for 10*Dq* is built from an ionic and a covalent part and the covalent contributions is directly related to the differences between the t_σ and t_π. Then, if in the final state the hopping is decreased, the covalent contribution to the crystal field splitting is also decreased. Conversely, decrease of the cubic crystal field splitting is a sign that the hopping is also decreased.

Further, the Coulomb repulsion U_{dd} is not necessarily identical in the final state. In atomic multiplet calculations the two electron integrals $\langle 3d,3d|1/r|3d,3d\rangle$ are calculated ab initio. It turns out in the final state of 2p XAS these integrals are increased by about 5–10% (see, for example, the table for the Slater integrals in ref. 64), hence the atomic (unscreened) value of U_{dd} will also be 5–10% larger. For this reason we expect the final state value of U_{dd} to be slightly larger than the value in the ground state. This can be summarized in the statement that the wavefunctions ϕ_d localize and interact more strongly with each other. A detailed study has been performed for the creation of an oxygen 1s core hole in the copper oxides [53]. Apart from the large effect of the core hole potential on the oxygen 2p-states (U_{cp}), the effect on the neighboring 3d-states (U_{cd}^{*}) was also considered (* denotes inter-electronic Coulomb repulsions). It was shown that there is an effect on the Coulomb repulsion of the neighboring sites. U_{dd} decreases from 4.1 to 3.7 eV, which agrees with the qualitative discussion given above: a core hole created on site increases U_{dd}, but a core hole created at a neighboring site decreases U_{dd}. Another finding of this study is that the hopping t_{pd} is significantly decreased from 0.43 to 0.20 eV, which is (qualitatively) a similar result to that found for the system Mn in CdTe discussed above.

To end this section, the conclusion is given that the final state effect on model parameters is crucial for our understanding of the electronic structure, particularly because uncertainties on this topic also make a detailed description of the ground state less accurate. There are theoretical and experimental indications that there are indeed significant final state effects, and it is concluded that this topic needs more attention.

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References and notes

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