High-Resolution X-ray Emission and X-ray Absorption Spectroscopy

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I. Introduction

In this review, high-resolution X-ray emission and X-ray absorption spectroscopy will be discussed. The focus is on the 3d transition-metal systems. To understand high-resolution X-ray emission and resonant X-ray emission, it is first necessary to spend some time discussing the X-ray absorption process. Section II discusses 1s X-ray absorption, i.e., the K edges, and section III deals with 2p X-ray absorption, the L edges. X-ray emission is discussed in, respectively, section IV on 1s2p and 2s3p X-ray emission and section V on 2p3s and 2p3d X-ray emission. Section VI focuses on magnetic dichroism effects, and in section VII selective X-ray absorption experiments are discussed.

To limit the scope of this review paper, many related topics (for example, EELS, XPS, and resonant photoemission, phonon-oriented inelastic X-ray scattering, and X-ray microscopy) will not be discussed. In addition, many aspects of X-ray absorption, such as reflection experiments, diffraction absorption fine structure, and related experiments, will remain untouched. EXAFS will be discussed very briefly, and its X-ray emission analogue EXEFS\textsuperscript{69,71} will not be discussed.

A. X-ray Absorption

X-ray absorption is a synchrotron-based characterization technique that can be divided into near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS). In recent years a number of books, book chapters, and review papers have been published on X-ray absorption analysis. NEXAFS spectroscopy by Stöhr deals in detail with the analysis of soft X-ray 1s XANES spectra.\textsuperscript{101} A recent review on soft X-ray XANES has been written by Chen.\textsuperscript{24} Hard X-ray XANES and EXAFS has been discussed in the book by Koningsberger and Prins.\textsuperscript{72} Rehr and Albers recently wrote a review on the theory of hard X-ray XANES and EXAFS.\textsuperscript{92} In the Encyclopaedia of Analytical Chemistry, a recent chapter on X-ray absorption has been written by Kawai.\textsuperscript{70}
In the X-ray absorption process, a core electron is excited to an empty state and, as such, X-ray absorption probes the unoccupied part of the electronic structure of the system. In the EXAFS region, the excited electron has significant kinetic energy and the matrix element can be rewritten into a single-electron matrix element by removing all electrons that are inactive in the transition itself; in other words, the initial state minus the core hole is removed from eq 1b. All electron rearrangements that take place when a core hole is excited to a continuum electron are neglected, the series of delta functions identifies with the density of states (ρ), and the X-ray absorption spectral shape becomes

$$I_{\text{XAS}} \sim |\langle \Phi | \hat{e} r | \phi \rangle|^2 \delta_{E_F - E_i - \hbar \omega}$$  \hspace{1cm} (1a)$$

The dipole matrix element dictates that the density of states has an orbital moment that differs by 1 from the core state ($\Delta L = \pm 1$), while the spin is conserved ($\Delta S = 0$). In the case of X-rays, the quadrupole transitions are some hundred times weaker than the dipole transitions and can be neglected in most cases. They will be discussed for the preedge region in section II.B. Because in the final state a core hole is present, the density of states should be calculated with a core hole present. In many cases, this approximation gives an adequate simulation of the XAS spectral shape.

### II. 1s Edge X-ray Absorption

1s X-ray absorption spectra can be accurately described with single-particle methods within density functional theory. This is in many cases true both for metal and ligand K-edge and band structure methods or multiple scattering calculations can be used. Following the final state rule, one calculates the distribution of empty states in the final state of the absorption process. Because band structure calculations are carried out in reciprocal space, it is involved to calculate the final state density of states. It would imply the use of (large) supercells to include the core hole. Therefore, the ground-state density of states is often compared directly with the X-ray absorption spectrum. Various methods exist to calculate the single-particle density of states, for example, LMTO, LSW, LAPW, and KKR.

A formally closely related though conceptually different method is the calculation of the X-ray absorption cross section by a real-space multiple scattering calculation. Multiple scattering is particularly appropriate for the calculation of the empty states that can be easily calculated for arbitrary large energies. Multiple scattering calculations are usually performed with the Green function approach, with the X-ray absorption cross section written as a correlation function. The Green function describes the propagation of the electron in the solid, which is scattered by the atoms surrounding the absorbing atom. Detailed accounts of the multiple scattering are given in refs 78, 84, 93, and 118.

Because multiple scattering is performed as a real-space cluster calculation, the calculations can relatively easily be carried out for any system, ordered crystals but also for surfaces, interfaces, enzymes, etc. In addition, the core hole potential on the absorbing atom can be added directly in multiple scattering. Another advantage of multiple scattering is that it can be performed in steps of growing cluster sizes, and it is an appealing picture to observe the changes in the theoretical spectra from the effects of increas-
ing the number of backscatterers or from varying the included scattering paths around the absorbing atom. It has been shown that the multiple scattering formalism and the band structure formalism indeed give equivalent results if worked out rigorously in their mathematical basis. For comparison to experiment, both band structure calculations and multiple scattering results will be treated on the same footing using the density of states picture for guidance.

A. Metal 1s X-ray Absorption Spectra

The 1s edges of the 3d transition metals have energies ranging from about 4 to 9 keV. They are often used for EXAFS analysis, and also their XANES spectra are often used in many applied research investigations. An overview of 1s XANES spectra of 3d transition-metal systems is given in ref 29. Metal 1s XANES spectra are traditionally interpreted with multiple scattering methods. Self-consistent full potential multiple scattering calculations have recently been carried out for TiO2 by Cabaret and co-workers. They show that with polarization-dependent calculations the complete spectral shape of TiO2 is nicely reproduced. In particular, the preedge region is also described correctly. It can be concluded that the 1s edges of 3d transition metals do correspond to the metal p-projected density of states.

In most applications, the systems studied are not well-known. The metal 1s edges do show fine structure and edge shifts that can be used without the explicit calculation of the density of states. Figures 1 and 2 show a number of Fe 1s XANES spectra from Westre and co-workers. The FeI and FeII halide spectra given at the top do show significant variations within a certain valence. Analysis of unknown iron complexes can be carried out by comparison to spectra of known systems. The FeIII edges are shifted to higher energy with respect to the FeII edges. The shift to higher energies with higher valence is a general phenomenon that can be used to determine the valence of 3d transition metals in unknown systems.

1. Metal 1s Edge Shifts

A nice example of the use of the metal 1s edge shifts was recently given by Bae and co-workers. They did experiments on iron porphyrins adsorbed on carbon in acid electrolytes and follow the iron K edge as a function of the potential. Figure 3 shows the iron K-edge spectra and Figure 4 plots the shifts in the edge energy. The intact iron porphyrin shows an edge jump of 2.0 eV, indicating a sudden valence change.

B. The Preedge Region

The preedge region of the transition-metal 1s edges has led to a number of debates regarding the quadrupole and/or dipole nature and possible excitonic effects. The preedge region is related to transitions to the 3d bands. Both direct 1s3d quadrupole transitions and dipole transitions to 4p character hybridized with the 3d band are possible. For the quadrupole transitions, the matrix elements are only about 1% of the dipole transition, but on the other hand,
the amount of 3d character is by far larger than the p character. This can make, depending on the particular system, the contributions of quadrupole and dipole transitions equivalent in intensity. A direct manner to check the nature of the transitions is to measure the polarization dependence, which is different for quadrupole and dipole transitions. 

The preedge region of iron compounds has systematically been investigated by Westre and co-workers. Some spectra are given in Figures 1 and 2. The preedges are analyzed in terms of quadrupole transitions, and analysis showed that the spectra should be interpreted in terms of multiplet theory, including the crystal field and the atomic interactions in LS coupling. This is an approximation to the multiplet calculations as carried out in ligand-field multiplet theory, as will be explained in section III.

Figure 3. Series of in situ Fe K-edge XANES for intact iron porphyrin at different potentials (A) and heat-treated FeTMPPCl/BP (B). (Reprinted with permission from ref 4. Copyright 1998 American Chemical Society.)

Figure 4. Plots of the edge energy versus the potential extracted from data of the type shown in Figure 3. (Reprinted with permission from ref 4. Copyright 1998 American Chemical Society.)

C. Ligand 1s X-ray Absorption

Oxygen, carbon, and nitrogen 1s X-ray absorption spectra have excitation energies between 300 and 700 eV, which is in the soft X-ray range. The interpretation of 1s spectra in the soft X-ray range has been dominated by band structure approaches because the details of the potential are crucial and until recently multiple scattering calculations did not reach good agreement. Figure 6a shows the density of states of rutile TiO$_2$. The total density of states has been separated into its oxygen and titanium contributions. The zero of energy is the top of the oxygen 2p valence band, which can be seen to have a significant titanium contribution. The two sharp peaks between
3 and 8 eV are the titanium 3d peaks. They relate to, respectively, the $t_{2g}$ and $e_g$ orbitals that are split by the cubic crystal field. Both have a significant oxygen contribution, indicating the covalent nature of TiO$_2$. The structures at 10 eV and higher are the titanium 4s and 4p bands plus all higher lying continuum states. These delocalized states have a similar density of states for oxygen and titanium.

Figure 6b compares the oxygen p-projected density of states with the 1s X-ray absorption spectra of rutile TiO$_2$. The spectral shape is reproduced, and if the broadening is further optimized, a close to perfect fit of the experiment can be obtained. It can be concluded that in TiO$_2$ the density of states as obtained from a ground-state calculation gives an accurate description of the oxygen 1s X-ray absorption spectral shape. This implies that the core hole potential does not have a large influence on the spectral shape.

Figure 5. Atomic and ligand-field multiplet calculations for the quadrupole transitions $3d^5 \rightarrow 1s^33d^6$ for Fe$^{II}$ (bottom) and $3d^6 \rightarrow 1s^33d^7$ for Fe$^{III}$ (top). The left spectra are the atomic multiplets; the right spectra have an additional cubic crystal field of 1.0 eV.

Figure 6. Right: comparison of the oxygen K-edge X-ray absorption spectra (---) with the oxygen p-projected density of states (---) for rutile TiO$_2$; left: unbroadened density of states of rutile TiO$_2$. (Reprinted with permission from ref 35. Copyright 1993 American Physical Society.)
agreement of the density of states with experiments shows, however, that multiplet effects are hardly (or not at all) visible in the spectrum.

For other ligands such as carbides, nitrides, and sulfides, a similar interpretation as that for oxides is expected to hold. Their ligand 1s X-ray absorption spectra are expected to show close comparison to the projected density of states, as confirmed by calculations.123

**III. 2p Edge X-ray Absorption**

In the case of 2p X-ray absorption (L edges), the single-particle approximation breaks down and the XANES structures are affected by the core hole wave function. The core hole and free electron of eq 1b are rewritten to a 2p core hole (2p) and a 3d electron. All valence electrons except the 3d electrons are omitted, and this yields eq 2b, which is the starting point for all calculations.

\[
I_{XAS} \sim |\langle \Phi_j | 2p_{3d} \hat{r} | \Phi_i \rangle|^2 \delta_{E_F - E_{1s - \text{metal}}} \quad (2a)
\]

\[
I_{XAS} \sim |\langle 2p_{3d}^{N+1} | \hat{r} | 3d^{N} \rangle|^2 \delta_{E_F - E_{1s - \text{metal}}} \quad (2b)
\]

This so-called multiplet effect will be discussed in some detail because it is an important effect for all 2p X-ray absorption, the 1s preedges, as well as all X-ray emission experiments.

**The Multiplet Effect.** The breakdown of the single-particle model is important in all systems with electrons in narrow bands, for example, the 3d metals and the rare-earth metals. In these systems the p and d core wave functions strongly overlap with the 3d and 4f, respectively, valence wave functions. This strong local interaction has to be considered in order to obtain an accurate description of the XANES spectral shape. A successful analysis method has been developed based on a ligand-field multiplet model.20 It offers large sensitivity to the valence and the symmetry of the element studied.

**A. Atomic Multiplet Theory**

The basic starting point for a large part of the analysis of core-level spectra is atomic multiplet theory.25,123 Faced with the situation of a solid with its combination of extended valence states and a localized core hole, the problem is to find the best way to treat the X-ray absorption process. A localized approach makes it possible to treat the core hole in detail, while an itinerant approach is in most cases the best approach to the ground state of the solid. In the following some aspects of atomic multiplet theory that are important for the analysis of X-ray absorption and X-ray emission spectra will be briefly introduced.

It has been shown over the last 30 years that a completely localized approach, based on atomic multiplet theory, can be very fruitful to core-level spectroscopy. In this section atomic multiplet theory will be developed. Some basic quantum-mechanic results of atomic theory will be partly repeated, but the focus will be on the specific problems of a core hole in a solid.
1. The Atomic Hamiltonian

The atomic Hamiltonian is given by the Schrödinger equation for an N-electron atom. The Schrödinger equation consists of the kinetic energy of the N electrons ($\sum \frac{p_i^2}{2m}$), the electrostatic interaction of the N electrons with the nucleus of charge +Z ($\sum_{N} -Ze^2/r_{i}$), the electron–electron repulsion ($H_{\text{ee}} = \sum_{\text{pairs}} e^2/r_{ij}$), and the spin–orbit coupling of each electron ($H_{\text{so}} = \sum_{N} \zeta(r_i) l_i \cdot s_i$). The overall Hamiltonian reads

$$H = \sum_{N} \frac{p_i^2}{2m} + \sum_{N} -\frac{Ze^2}{r_i} + \sum_{\text{pairs}} \frac{e^2}{r_{ij}} + \sum_{N} \zeta(r_i) l_i \cdot s_i \quad (3a)$$

The kinetic energy and the interaction with the nucleus are the same for all electrons in a certain atomic configuration, for example, 3d$^2$ in the case of Mn$^{11}$. They define the average energy of a certain state ($H_{\text{av}}$). This leaves the electron–electron repulsion and the spin–orbit coupling as the important interactions. The basic difficulty when solving the Schrödinger equation is that $H_{\text{ee}}$ is too large to be treated as a perturbation. This problem has been solved with the central field approximation, in which the spherical average of the electron–electron interaction is separated from the nonspherical part. The spherical average ($H_{\text{ee}}$) is added to $H_{\text{av}}$ to form the average energy of a configuration. In the modified electron–electron Hamiltonian $H'_{\text{ee}}$, the spherical average has been subtracted.

$$H'_{\text{ee}} = H_{\text{ee}} - \langle H_{\text{ee}} \rangle = \sum_{\text{pairs}} \frac{e^2}{r_{ij}} - \left( \sum_{\text{pairs}} \frac{e^2}{r_{ij}} \right) \quad (3b)$$

This leaves the two interactions $H'_{\text{ee}}$ and $H_{\text{so}}$ to determine the energies of the various electronic symmetry configurations within the atomic configuration.

2. Term Symbols

Electronic symmetry configurations are indicated with their orbital moment L, spin moment S, and total moment J. Together, these three quantum numbers indicate a certain state and determine its specific energy. If spin–orbit coupling is neglected, all configurations with the same L and S moments have the same energy. A specific configuration is indicated by a so-called term symbol $2S + 1L_J$. A term symbol gives all three quantum numbers and as such determines the symmetry and energy of a certain configuration. A single 1s electron has an orbital moment L = 0, a spin moment S = 1/2, and a total moment J = 1/2. This is written with a term symbol as $^1S_{1/2}$. A 2p electron has two possible symmetries depending on the spin–orbit coupling, $^2P_{1/2}$ and $^2P_{3/2}$. These two configurations are related, respectively, the L$_2$ and the L$_3$ edge in 2p X-ray absorption. In the case of a transition-metal ion, the important initial state configurations are 3d$^n$. In the final state with a 3s or a 3p core hole, the important configurations are 3s$^2$3d$^n$ and 3p$^2$3d$^n$. The main quantum number does not influence the coupling schemes, so exactly the same term symbols can be found for 4d and 5d systems and for 2s and 2p core holes.

A 3d$^2$ configuration is 10-fold degenerate and has the term symbols $^4D_{5/2}$ and $^4D_{3/2}$ with, respectively, six and four electrons. The degeneracy of a term symbol $2S + 1L_J$ is given as $2J + 1$. The overall degeneracy of a term symbol $2S + 1L_J$ is $(2S + 1)(2L + 1)$. The LS term symbols of a 3d$^4$d$^1$ configuration can be found by multiplying $^2D \otimes D$. The multiplication of L and S is independent, and one finds that the total orbital moment L is equal to 0, 1, 2, 3, or 4. S is equal to 0 or 1. This gives the term symbols as indicated in Table 1. The total degeneracy of the 3d$^4$d$^1$ configuration is 100, which can be checked by adding the degeneracies of the 10 term symbols. After inclusion of spin–orbit coupling, a total of 18 2$^{25+1}L_J$ term symbols is found.

A 3d$^2$ configuration does not have a degeneracy of 100. The Pauli exclusion principle forbids two 3d electrons to have the same quantum numbers, which has the consequence that the second electron has not 10 but only 9 possible states. In addition, the sequence of the quantum states for the two electrons makes no difference, which divides the number of different two-electron states by two. This gives 10 × 9/2 = 45 possible states. One can write out all 45 combinations of a 3d$^2$ configuration and sort them by their M_L and M_S quantum numbers. Analysis of the combinations of the allowed M_L and M_S quantum numbers yields the term symbols $^1G$, $^3F$, $^1D$, $^3P$, and $^1S$. This is a subset of the term symbols of a 3d$^4$d$^1$ configuration. The term symbols can be divided into their J quantum numbers as $^3F_2$, $^3F_3$, $^3F_4$, $^3P_0$, $^3P_1$, $^3P_2$, $^1G_4$, $^1D_2$, and $^1S_0$. In the case of a 3d$^3$ configuration, a similar approach gives that the possible spin states are doublet and quartet. The quartet states have all spins parallel, and the Pauli principle implies that there are two quartet term symbols, respectively, $^4F$ and $^4P$. The doublet states have two electrons parallel, and for these two electrons, the Pauli principle yields the combinations identical to the triplet states of the 3d$^2$ configuration. To these two parallel electrons a third electron is added antiparallel, where this third electron can have any value of its orbital quantum number m. Writing out all combinations and separating them into the total orbital moments M_L gives the doublet term symbols $^2H$, $^2G$, $^2F$, $^2D$, another $^2D$, and $^2P$. By adding the degeneracies, it can be checked that a 3d$^4$ configuration has 120 different states, i.e., 10 × 9/2 × 8/3. The general formula to determine the degeneracy of
A 3d\(^n\) configuration is
\[
\binom{10}{n} = \frac{10!}{(10-n)!n!}
\]
(4)

A new result with respect to the s and p electrons is that one finds for a 3d\(^3\) configuration two states with an identical term symbol. To distinguish both term symbols, the so-called seniority number is introduced. The seniority number is the number \(N\) of the 3d\(^N\) configuration for which a term symbol occurs first. For example, the 2\(^D\) term symbol occurs for a 3d\(^1\) configuration; hence, it has seniority number 1. The term symbol could be rewritten as 3\(^D\). The second 2\(^D\) term symbol of 3d\(^3\) takes its seniority number from the next lowest number \(N\) and is written as 3\(^D\). The discussion of the seniority number brings us to another observation, which is that the term symbols of a configuration 3d\(^N\) do also exist in a configuration 3d\(^{N+2}\) as well. Thus, the term symbols of 3d\(^4\) contain all term symbols of 3d\(^2\), which contains the 1S term symbol of 3d\(^0\). Similarly, the term symbols of 3d\(^5\) contain all term symbols of 3d\(^3\), which contains the 2\(^D\) term symbol of 3d\(^1\). In addition, there is a symmetry equivalence of holes and electrons; hence, 3d\(^3\) and 3d\(^7\) states with the Hamiltonian
\[
H = \sum_l \sum_{ij} \epsilon_{ij} r_{ij} + \sum_{l} \xi(r_l) l^2 s_l
\]
(6)

The electron-electron interaction commutes with \(L^2\), \(S^2\), \(L_z\), and \(S_z\), which implies that all off-diagonal elements are zero. A simple example is a 1s2s configuration consisting of \(3^S\) and \(3^S\) term symbols. The respective energies can be shown to be
\[
\langle 1S | \frac{\epsilon^2}{r_{12}} | 1S \rangle = F^0 (1s2s) + G^0 (1s2s)
\]
(7)
\[
\langle 3S | \frac{\epsilon^2}{r_{12}} | 3S \rangle = F^0 (1s2s) - G^0 (1s2s)
\]
(8)

\(F^0\) and \(G^0\) are the Slater–Condon parameters for, respectively, the direct Coulomb repulsion and the Coulomb exchange interaction. The main result can be stated as “the singlet and the triplet state are split by the exchange interaction”. This energy difference is 2\(G^0\) (1s2s). An analogous result is found for a 1s2p state for which the singlet and triplet states are split by 2/3\(G^0\) (1s2p). The 2/3 prefactor is determined by the degeneracy of the 2p state. The general formulation of the matrix elements of two-electron wave functions can be written as
\[
\langle 2S+1L_J | \frac{\epsilon^2}{r_{12}} | 2S+1L_J \rangle = \sum_k f_k F_k \sum_k g_k G_k
\]
(9)

To obtain this result, the radial parts \(F_k\) and \(G_k\) have been separated using the Wigner-Eckardt theorem and Hamiltonian \(1/\rJ\) has been expanded in a series.\(^{123}\) The angular parts \(f_k\) and \(g_k\) can be calculated using angular momentum coupling, and the result is written in terms of \(3j\) and \(6j\) symbols
\[
f_k = (2l_1 + 1)(2l_2 + 1)(-1)^k \begin{pmatrix} l_1 & k & l_1 \end{pmatrix} \begin{pmatrix} l_2 & k & l_2 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \end{pmatrix}
\]
(10)
\[
g_k = (2l_1 + 1)(2l_2 + 1)(-1)^k \begin{pmatrix} l_1 & k & l_2 \end{pmatrix} \begin{pmatrix} l_2 & k & l_1 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \end{pmatrix}
\]
(11)

For equivalent electrons, \(g_k\) is not present and \(f_k\) can be simplified by setting \(l_1 = l_2 = l\). The values of \(k\) can be determined from the so-called triangle conditions of the \(3j\) symbols. The triangle conditions imply that for \(3j\) symbols with all zeros for \(m_l\) (given in the bottom row), the sum of the \(j\) values (given in the top row) must be even and that the maximum \(j\) value is equal to the sum of the two others. Using the two \(3j\) symbols of eqs 10 and 11, this implies for \(f_k\) that \(k\) must always be even. \(k = 0\) is always present, and the maximum value for \(k\) equals two times the lowest value of \(l\). For \(g_k\), it implies that \(k\) is even if \(l_1 + l_2\) is even and \(k\) is odd if \(l_1 + l_2\) is odd. The maximum value of \(k\) equals \(l_1 + l_2 + 2\). Table 2 gives the possible \(k\) values for some important configurations.

Table 2: Possible Values of \(k\) for the Angular Coefficients \(f_k\) and \(g_k\)

<table>
<thead>
<tr>
<th>conf.</th>
<th>(f_k)</th>
<th>(g_k)</th>
<th>conf.</th>
<th>(f_k)</th>
<th>(g_k)</th>
<th>conf.</th>
<th>(f_k)</th>
<th>(g_k)</th>
<th>conf.</th>
<th>(f_k)</th>
<th>(g_k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s^2</td>
<td>0</td>
<td>1s2s</td>
<td>0</td>
<td>0</td>
<td>1s2p</td>
<td>0</td>
<td>1</td>
<td>2p^2</td>
<td>0.2</td>
<td>2p3p</td>
<td>0.2</td>
</tr>
<tr>
<td>2p^2</td>
<td>0.2</td>
<td>2p3p</td>
<td>0.2</td>
<td>0.2</td>
<td>2p3d</td>
<td>0.2</td>
<td>1.3</td>
<td>3d^3</td>
<td>0.24</td>
<td>3d4d</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The energies of the representations of the 3d\(^2\) configuration are calculated. First, it can be shown that \(f_0\) is equal to the number of permutations \((n(n
- 1)/2) of n electrons, i.e., \( f_0 \) is equal to 1.0 for two-electron configurations. The electrons come from the same shell; hence, there are no exchange interactions. One is left with the calculation of \( f_2 \) and \( f_4 \) for the five term symbols \( 1S \), \( 3P \), \( 1D \), \( 3F \), and \( 1G \), which implies that the prefactor \( (2l_1 + 1)(2l_2 + 1) \) is equal to 25. The \( 3j \) symbols are only dependent on \( k \) and are equal to \( \sqrt{2/35} \). For all five states this gives a prefactor of \( 25 \times 2/35 = 10/7 \), i.e., \( f_4 \) is equal to

\[
f_k = \frac{10}{7} \left( \frac{2}{2} \right), (-1)^l \quad (12)
\]

The Slater–Condon parameters \( F^2 \) and \( F^4 \) have approximately a constant ratio: \( F^4 \approx 0.62F^2 \). The last column in Table 3 gives the approximate energies of the five term symbols. In case of the 3d transition-metal ions, \( F^2 \) is approximately equal to 10 eV. For the five term symbols this gives the energies as \( F^2 \) at \(-1.8 \) eV, \( 1D \) at \(-0.1 \) eV, \( 3P \) at \(+0.2 \) eV, \( 1G \) at \(+0.8 \) eV, and \( 1S \) at \(+4.6 \) eV. The \( 3F \) term symbol has lowest energy and is the ground state of a 3d\(^2\) system. This is in agreement with Hund’s rules, which will be discussed in the next section. The three states \( 1D \), \( 3P \), and \( 1G \) are close in energy, 1.7–2.5 eV above the ground state. The \( 1S \) state has a high energy of 6.3 eV above the ground state, the reason being that two electrons in the same orbit strongly repel each other.

Table 3: Energies of the Five Term Symbols of a 3d\(^2\) Configuration. The Energy in the Last Column Is Calculated Using the Approximation that the Radial Integrals \( F^2 \) and \( F^4 \) Have a Constant Ratio of 0.62

<table>
<thead>
<tr>
<th>( f_2 )</th>
<th>( f_4 )</th>
<th>energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1S )</td>
<td>( \left( \frac{2}{2} \right) )</td>
<td>( \frac{27}{7} )</td>
</tr>
<tr>
<td>( 3P )</td>
<td>( \left( \frac{2}{2} \right) )</td>
<td>( \frac{3}{7} )</td>
</tr>
<tr>
<td>( 1D )</td>
<td>( \left( \frac{2}{2} \right) )</td>
<td>( \frac{3}{49} )</td>
</tr>
<tr>
<td>( 3F )</td>
<td>( \left( \frac{2}{2} \right) )</td>
<td>( -8/49 )</td>
</tr>
<tr>
<td>( 1G )</td>
<td>( \left( \frac{2}{2} \right) )</td>
<td>( 4/49 )</td>
</tr>
</tbody>
</table>

the five term symbols. In case of the 3d transition-metal ions, \( F^2 \) is approximately equal to 10 eV. For the five term symbols this gives the energies as \( F^2 \) at \(-1.8 \) eV, \( 1D \) at \(-0.1 \) eV, \( 3P \) at \(+0.2 \) eV, \( 1G \) at \(+0.8 \) eV, and \( 1S \) at \(+4.6 \) eV. The \( 3F \) term symbol has lowest energy and is the ground state of a 3d\(^2\) system. This is in agreement with Hund’s rules, which will be discussed in the next section. The three states \( 1D \), \( 3P \), and \( 1G \) are close in energy, 1.7–2.5 eV above the ground state. The \( 1S \) state has a high energy of 6.3 eV above the ground state, the reason being that two electrons in the same orbit strongly repel each other.

Table 4: Relations between the Slater–Condon Parameters and Racah Parameters. The Top Half Gives the Relationships between the Three Parameter Sets. The Bottom Half Uses \( F^0 = 8.0 \) eV, \( F^2 = 10.0 \) eV, and \( F^4 = 6.2 \) eV

<table>
<thead>
<tr>
<th>Slater–Condon</th>
<th>normalized</th>
<th>Racah</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F^0 )</td>
<td>( F_0 = F^0 )</td>
<td>( A = F_0 - 49F_4 )</td>
</tr>
<tr>
<td>( F^2 )</td>
<td>( F_2 = F^{2/49} )</td>
<td>( B = F_2 - 5F_4 )</td>
</tr>
<tr>
<td>( F^4 )</td>
<td>( F_4 = F^{4/441} )</td>
<td>( C = 35F_4 )</td>
</tr>
<tr>
<td>( F^0 = 8.0 )</td>
<td>( F_0 = 8.0 )</td>
<td>( A = 7.3 )</td>
</tr>
<tr>
<td>( F^2 = 10.0 )</td>
<td>( F_2 = 0.41 )</td>
<td>( B = 0.13 )</td>
</tr>
<tr>
<td>( F^4 = 6.2 )</td>
<td>( F_4 = 0.014 )</td>
<td>( C = 0.49 )</td>
</tr>
</tbody>
</table>

finding of the \( 3F \) state as the ground state of a 3d\(^2\) configuration is an example of the so-called Hund’s rules. On the basis of experimental information, Hund did formulate three rules to determine the ground state of a 3d\(^2\) configuration. The Hund rules are as follows: (1) term symbol with maximum spin \( S \), (2) term symbol with maximum orbital moment \( L \), and (3) term symbol with maximum total moment \( J \), if the shell is more than half full.

A configuration has the lowest energy if the electrons are as far apart as possible. Hund’s first rule of ‘maximum spin’ can be understood from the Pauli principle: Electrons with parallel spins must be in different orbitals, which overall implies larger separations, hence lower energies. This is, for example, evident for a 3d\(^5\) configuration, where the \( 6S \) state has its five electrons divided over the five spin-up orbitals, which minimizes their repulsion. In case of 3d\(^7\), Hund’s first rule implies that either the \( 3P \) or \( 3F \) term symbol must have the lowest energy. From the previous section, one finds that the \( 3F \) term symbol is lower than the \( 3P \) term symbol, the reason being that the \( 3F \) wave function tends to minimize electron repulsion. The effects of spin–orbit coupling are well-known in the case of core states. Consider, for

4. Atomic Multiplet Ground States of 3d\(^n\) Systems

The ground-state symmetries of the transition-metal compounds that are characterized with a partly filled 3d band will be discussed. The term symbols with the lowest energy are found after calculating the matrix elements. The term symbols found to be at the lowest energy are indicated in Table 5. The

Table 5: 2p X-ray Absorption Transitions from the Atomic Ground State to All Allowed Final-State Symmetries, after Applying the Dipole Selection Rule: \( \Delta J = -1, 0, \) or \(+1\)

<table>
<thead>
<tr>
<th>transition</th>
<th>no. of term symbols: ground state</th>
<th>symmetry: ground state</th>
<th>no. of term symbols: final state</th>
<th>no. of allowed transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^4 )</td>
<td>1 ( ^1S_0 )</td>
<td>12</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^5 )</td>
<td>2 ( ^4S_{2} )</td>
<td>49</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^6 )</td>
<td>3 ( ^4D_5 )</td>
<td>95</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^4 )</td>
<td>4 ( ^4F_{5/2} )</td>
<td>180</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^5 )</td>
<td>5 ( ^4D_{2} )</td>
<td>205</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^6 )</td>
<td>6 ( ^4S_{5/2} )</td>
<td>110</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^7 )</td>
<td>7 ( ^4D_{2} )</td>
<td>110</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^8 )</td>
<td>8 ( ^4F_{5/2} )</td>
<td>45</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^9 )</td>
<td>9 ( ^4F_{4} )</td>
<td>12</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>( 3d^2 \rightarrow 2p^3d^{10} )</td>
<td>10 ( ^2D_{5/2} )</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>
example, the 2p XAS or XPS spectrum of nickel. The $^{2}P_{3/2}$ peak is positioned at approximately 850 eV and the $^{2}P_{1/2}$ at about 880 eV, where the state with the lowest binding energy is related to the lowest energy of the configuration. The case of the 2p core state is an example of d Hund’s third rule: the configuration is $2p^5$, which is more than half-full, implying that the highest $J$ value has the lowest energy. The third rule implies that the ground state of a 3d$^0$ configuration is $^3F_4$, while it is $^3P_2$ in the case of a 3d$^2$ configuration.

5. X-ray Absorption Spectra Described with Atomic Multiplets

I will start with the description of closed-shell systems. The 2p X-ray absorption process excites a 2p core electron into the empty 3d shell, and the transition can be described as $2p^53d^0 \rightarrow 2p^43d^1$. The ground state has $^1S_0$ symmetry, and it is found that the term symbols of the final state are $^1P_1$, $^1D_2$, $^1F_3$, $^3P_{012}$, $^3D_{123}$, and $^3F_{234}$. The energies of the final states are affected by the 2p3d Slater–Condon parameters, the 2p spin–orbit coupling, and the 3d spin–orbit coupling. The X-ray absorption transition matrix elements to be calculated are

$$I_{\text{XAS}} \propto \langle 3d^0 | | 2p^53d^1 \rangle^2$$  \hspace{1cm} (13a)

The symmetry aspects are

$$I_{\text{XAS}} \propto \langle |^1S_0 \rangle | |^1P_1 \rangle | |^1\text{PDF} \rangle^2$$  \hspace{1cm} (13b)

The symmetry of the dipole transition is given as $^1P_1$, according to the dipole selection rules, which state that $\Delta J = +1, 0, -1$. Within LS coupling, also $\Delta S = 0$ and $\Delta L = 1$. The dipole selection rule reduces the number of final states that can be reach from the ground state. The J value in the ground state is zero. In this case, the dipole selection rule proclaims that the J value in the final state must be 1; thus, only the three term symbols $^1P_1$, $^3P_1$, and $^3D_1$ can obtain finite intensity. The problem of calculating the 2p absorption spectrum is reduced to solving the $3 \times 3$ energy matrix of the final states with $J = 1$. As discussed above, the atomic energy matrix consists of terms related to the two-electron Slater integrals and the 2p and 3d spin–orbit couplings.

A series of X-ray absorption spectra of tetravalent titanium 2p and 3p edges and the trivalent lanthanum 3d and 4d edges is compared. The ground states of Ti$^{IV}$ and La$^{III}$ are, respectively, 3d$^0$ and 4f$^0$, and they share a $^1S_0$ ground state. The transitions at the four edges are, respectively

- Ti$^{IV}$ L$_{2,3}$ edge: $3d^0 \rightarrow 2p^53d^1$
- Ti$^{IV}$ M$_{2,3}$ edge: $3d^0 \rightarrow 3p^53d^1$
- La$^{III}$ M$_{4,5}$ edge: $4f^0 \rightarrow 3d^94f^4$
- La$^{III}$ N$_{4,5}$ edge: $4f^0 \rightarrow 4d^94f^4$

These four calculations are equivalent, and all spectra consist of three peaks with $J = 1$ as described above in the case of the 2p edge of Ti$^{IV}$. The things that change are the values of the atomic Slater–Condon parameters and core hole spin–orbit couplings. They are given in Table 6 for the four

<table>
<thead>
<tr>
<th>Edge</th>
<th>Ti 2p</th>
<th>Ti 3p</th>
<th>La 3d</th>
<th>La 4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average energy (eV)</td>
<td>464</td>
<td>37</td>
<td>840</td>
<td>103</td>
</tr>
<tr>
<td>Core spin–orbit (eV)</td>
<td>3.78</td>
<td>0.43</td>
<td>6.80</td>
<td>1.12</td>
</tr>
<tr>
<td>$F^2$ Slater–Condon (eV)</td>
<td>5.04</td>
<td>8.91</td>
<td>5.65</td>
<td>10.45</td>
</tr>
</tbody>
</table>

Table 6: Relative Intensities, Energy, Core Hole Spin–Orbit Coupling, and $F^2$ Slater–Condon Parameters Are Compared for Four Different $^1S_0$ Systems

<table>
<thead>
<tr>
<th></th>
<th>Ti 2p</th>
<th>Ti 3p</th>
<th>La 3d</th>
<th>La 4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative intensities</td>
<td>10$^{-2}$</td>
<td>10$^{-4}$</td>
<td>10$^{-2}$</td>
<td>10$^{-3}$</td>
</tr>
<tr>
<td>p$<em>{3/2}$ or d$</em>{3/2}$</td>
<td>0.72</td>
<td>10$^{-3}$</td>
<td>0.80</td>
<td>10$^{-2}$</td>
</tr>
<tr>
<td>p$<em>{1/2}$ or d$</em>{5/2}$</td>
<td>1.26</td>
<td>1.99</td>
<td>1.19</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Figure 8. Atomic multiplet calculations for the 3d$^0$ and 4f$^0$ ions Ti$^{IV}$ and La$^{III}$. Given are the transitions 3d$^0 \rightarrow 2p^53d^1$, 3d$^0 \rightarrow 3p^53d^1$, 4f$^0 \rightarrow 3d^94f^4$, and 4f$^0 \rightarrow 4d^94f^4$. All spectra are shown on a logarithmic scale to make the prepeaks clearly visible.

Figure 8 shows the X-ray absorption spectral shapes. They are given on a logarithmic scale to make the preedges visible.

In Table 5 the term symbols of all 3d$^0$ systems are given. Together with the dipole selection rules, this sets immediately strong limits to the number of final states which can be reached, similar to the case of a 3d$^0$ ground state. Consider, for example, the 3d$^0 \rightarrow 2p^53d^1$ transition: The 3d$^0$ ground state has $J = 3/2$ and there are, respectively, 21, 35, and 39 states of 2p$^5$3d$^1$ with $J' = 1/2$, $J' = 3/2$, and $J' = 5/2$. This
implies a total of 95 allowed peaks out of the 180 final-state term symbols. From Table 5 some special cases can be discriminated: a 3d⁰ system makes a transition to a 2p⁵3d¹ configuration, which has only two term symbols, out of which only the term symbol with \( J' = 3/2 \) is allowed. In other words, the L₂ edge has zero intensity. 3d⁰ and 3d⁸ systems have only three and four peaks, respectively, because of the limited amount of states for the 2p⁵3d⁰ and 2p⁵3d⁸ configurations.

Atomic multiplet theory is able to accurately describe the 3d and 4d X-ray absorption spectra of the rare earth metals. In the case of the 3d metal ions, atomic multiplet theory cannot simulate the X-ray absorption spectra accurately because the effects of the neighbors on the 3d states are too large. It turns out that it is necessary to include both the symmetry effects and the configuration-interaction effects of the neighbors explicitly. Ligand-field multiplet theory takes care of all symmetry effects, while charge-transfer multiplet theory allows the use of more than one configuration.

**B. Ligand-Field Multiplet Theory**

If one transfers this atomic method to the solid state, two questions that arise 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. This has been used particularly to describe the optical absorption spectra of transition-metal ions. For core spectroscopies, ligand-field theory has been developed by Thole and co-workers. The effects of itinerant states on multiplets will be described using the charge-transfer multiplet approach as described in the next section.

The dominant symmetry effect in solids is the cubic ligand field. The strength of this operator is usually denoted as the ligand-field splitting (10Dq). Atomic multiplet theory can be extended to describe the 3d metal ions by incorporation of the ligand-field splitting. In an octahedral environment, the field of the neighboring atoms on the of the central atom has cubic (O₆) symmetry which divides the 5-fold-degenerate 3d orbitals into two distinct representations of T₂g and E_g symmetry. The 2-fold-degenerate E_g state contains orbitals that point toward the center of the cube faces, which is directly toward the position of the ligands. Consequently, E_g states interact stronger, electrostatically as well as covalently, with the ligands. The three T₂g orbitals point toward the corners of the cube, and therefore, their interaction with the octahedral ligands is smaller.

The effect of the cubic ligand field on the energies of the atomic states has been described in the textbooks of Ballhausen, Griffith, and Sugano, Tanabe, and Kitamura. It is found that the degeneracy of the atomic states is partially lifted and the D, F, and higher states are split into a series of representations in cubic symmetry. In the 2p⁵3d⁰ final state, the effects of the cubic ligand field are equivalent to that in the initial state. A difference is that the number of multiplet states is considerably larger: For a 3d⁰ initial state, the maximum number of states is 256, while it is six times larger (1512) for a 2p⁵3d⁰ final state.

The transition probability for the 3d⁰ systems in cubic symmetry is

\[
W \propto \langle 3d^0|A_1|p[T_1]|2p^53d^1[T_1]\rangle^2
\]

All final states of T₁ symmetry are allowed and have a finite transition probability from the A₁ initial state. This includes the states of J = 1 atomic symmetry and additionally the atomic states with J = 3 and J = 4. The degeneracy of these states is, respectively, 3 and 1. The total number of allowed final states in cubic symmetry is \( 3 + 3 + 1 = 7 \). Figure 9 shows the effects of an increasing cubic ligand field on the multiplet spectrum of the 3d⁰ \( \rightarrow \) 2p⁵3d⁰ transition. In this figure it can be seen that for small values of the ligand field (the step size is 0.3 eV) the spectrum is hardly modified. For small values of 10Dq, the four states which were forbidden in atomic symmetry have not gained enough intensity to be detectable in the spectrum. The peak splitting in the spectrum is related to the value of 10Dq, but it is not a direct measure of it. This implies that one cannot measure the crystal-field splitting directly in a 2p X-ray absorption spectra.

The ligand-field multiplet results as calculated with the procedure outlined above can be directly compared with experiment. Figure 10 compares the ligand-field multiplet calculation of CaF₂ with the 2p X-ray absorption spectrum of CaF₂. Atomic Slater integrals were used. For details, see refs 37 and 38. All peaks in the experimental spectrum are reproduced, which is a confirmation that the ligand-field multiplets indeed dominate the spectral shape. When resonant X-ray emission will be discussed, CaF₂ will be used as an example of what happens if one excites to these multiplet peaks.
Table 7: Projection of the 2p X-ray Absorption Transitions from Atomic Symmetry (SO) to Octahedral Symmetry (Oh). Degeneracies of the Configurations Are Given. The Last Column Gives the Degeneracies without Any Symmetry (C1).

<table>
<thead>
<tr>
<th>transition</th>
<th>degeneracies in spherical symmetry</th>
<th>degeneracies in octahedral symmetry</th>
<th>degeneracies without symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d⁰ → 2p³3d⁴</td>
<td>1 → 12</td>
<td>1 → 25</td>
<td>1 → 60</td>
</tr>
<tr>
<td>3d⁰ → 2p³3d⁵</td>
<td>2 → 45</td>
<td>3 → 90</td>
<td>10 → 270</td>
</tr>
<tr>
<td>3d⁰ → 2p³3d⁶</td>
<td>9 → 110</td>
<td>20 → 300</td>
<td>45 → 720</td>
</tr>
<tr>
<td>3d⁰ → 2p³3d⁷</td>
<td>19 → 180</td>
<td>39 → 420</td>
<td>120 → 1260</td>
</tr>
<tr>
<td>3d⁰ → 2p³3d⁸</td>
<td>34 → 205</td>
<td>91 → 630</td>
<td>210 → 1512</td>
</tr>
<tr>
<td>3d⁰ → 2p³3d⁹</td>
<td>37 → 180</td>
<td>86 → 420</td>
<td>252 → 1260</td>
</tr>
<tr>
<td>3d⁰ → 2p³3d¹⁰</td>
<td>34 → 310</td>
<td>91 → 300</td>
<td>210 → 720</td>
</tr>
<tr>
<td>3d¹ → 2p³3d⁴</td>
<td>19 → 45</td>
<td>39 → 90</td>
<td>120 → 270</td>
</tr>
<tr>
<td>3d¹ → 2p³3d⁵</td>
<td>9 → 12</td>
<td>20 → 25</td>
<td>45 → 60</td>
</tr>
<tr>
<td>3d² → 2p³3d³</td>
<td>2 → 2</td>
<td>3 → 2</td>
<td>10 → 6</td>
</tr>
</tbody>
</table>

Table 7 gives the ground-state symmetries of the atomic multiplets and their projection to cubic symmetry. If four electrons have to be accommodated in the 3d orbitals in an octahedral surrounding, two effects are important: The exchange coupling of two 3d electrons (J) and the cubic ligand-field splitting (D). The exchange coupling is connected to the Slater integrals: \( J = (F^2 + F^4)/14 \), where the difference between the exchange couplings of \( e_g \) and \( t_{2g} \) electrons is neglected.\(^{30}\) If \( |J| > D \), a high-spin configuration with \( \Sigma_5 \) symmetry is formed from the Hund's rule \( \Sigma_5 \) ground state. If \( |J| < D \), a low-spin configuration with \( \Sigma_1 \) T₁ symmetry is formed. It can be checked that the same criterion applies to a \( \Sigma_3 \) configuration, while for \( \Sigma_6 \) and \( \Sigma_7 \) configurations, one should compare \( 2|J| \) with \( D \). The exchange coupling \( J \) is about 0.8 eV for 3d electrons, implying a high-spin low-spin transition point of approximately 2.4 eV for \( \Sigma_6 \) and \( \Sigma_7 \) and 1.8 eV for \( \Sigma_3 \) and \( \Sigma_7 \).

The calculation of the ligand-field multiplet spectrum is equivalent to that of the 3d⁰ configuration, with the additional possibility of low-spin ground states. To obtain the 2p X-ray absorption spectra, the calculated line spectrum is broadened with a Lorentzian broadening to simulate lifetime effects and a Gaussian broadening to simulate the resolution function of the experiment. Figure 11 shows the comparison for MnO. Excellent agreement is obtained with the atomic values of the Slater integrals and a ligand-field splitting of 0.8 eV. Or, to be more specific, the Slater integrals have been calculated by Hartree–Fock, and these Hartree–Fock values have been reduced to 80% of their calculated value. This procedure reproduces the experimental Slater integrals of atomic spectra. In the case of covalent systems, further reduction of the Slater integrals (according to the nephelauxetic effect) is often used. If one uses the charge-transfer multiplet model, charge transfer should take care of the effective reduction of Slater integrals. For more details, the reader is referred to refs 27 and 29 and references therein.

The transition from a high-spin to a low-spin ground state is directly visible in the spectral shape, because a different final-state multiplet is reached. This is shown theoretically and experimentally for a series of MnII compounds by Cramer and co-workers.\(^{26} \) An important advantage of soft X-ray edges is their high resolution, which can be less than 0.1 eV due to the long lifetime of the core states. The high resolution makes the spectra sensitive to details of the electronic structure, such as the valence, symmetry, spin state, and crystal-field value.\(^{26,29} \) It is important to realize that multiplet effects are a general phenomenon in all cases where a 2s, 2p, or 3p core hole is present in a 3d metal.

C. Charge-Transfer Multiplet Theory

The essence of the charge-transfer model is the use of two or more configurations. Ligand-field multiplet calculations use one configuration for which it solves the effective atomic Hamiltonian plus the ligand-field Hamiltonian, so essentially the following matrices

\[
\begin{align*}
I_{\text{XAS},1} & \propto \langle 3d^n|p|2p^{5}3d^{n+1}\rangle^2 \\
H_{\text{INT},1} & = \left( 3d^n | e^2_{12} + \zeta d^* s + H_{\text{LFM}} | 3d^n \right) \\
H_{\text{FINAL},1} & = \left( 2p^{5}3d^{n+1} | e^2_{12} + \zeta p^* s_p + \zeta d^* s_d + H_{\text{LFM}} | 2p^{5}3d^{n+1} \right)
\end{align*}
\]

The charge-transfer model adds a configuration \( 3d^{n+1}L \) to the \( 3d^n \) ground state. In the case of a transition-metal oxide, in a \( 3d^{n+1}L \) configuration an electron has been moved from the oxygen 2p valence band to the metal 3d band. The energy difference between the \( 3d^n \) and \( 3d^{n+1}L \) configurations is the so-
called charge-transfer energy ($\Delta$). One can continue with this procedure and add a 3d$^{n+1}$L$^2$ configuration, etc. In many cases two configurations will be enough to explain the spectral shapes, but in particular for high valence states, it can be important to include more configurations.\textsuperscript{45,80} The 3d states are described in a correlated fashion, while all other electrons are described in a band-like fashion.\textsuperscript{125} This is essentially the Anderson impurity model. The actual calculations can be carried out for a cluster or a quasiatomic model.

As far as X-ray absorption and X-ray emission are concerned, the consequences for the calculations are the replacement of 3d$^8$ with 3d$^8$ + 3d$^{n+1}$L plus the corresponding changes in the final state. This adds a second initial state, final state, and dipole transition

\begin{equation}
I_{\text{XAS,2}} \propto \langle \text{3d}^{n+1}L | \rho | 2p^5 \text{3d}^{n+2}L \rangle^2 \tag{15d}
\end{equation}

\begin{equation}
H_{\text{INIT,2}} = \left( \text{3d}^{n+1}L \right| \frac{\epsilon^2}{r_{12}} + \zeta_d l_d s_d + H_{\text{LFM}} \left| \text{3d}^{n+1}L \right\rangle \tag{15e}
\end{equation}

\begin{equation}
H_{\text{FINAL,2}} = \left( 2p^5 \text{3d}^{n+2}L \right| \frac{\epsilon^2}{r_{12}} + \zeta_d l_d s_d + H_{\text{LFM}} \left| 2p^5 \text{3d}^{n+2}L \right\rangle \tag{15f}
\end{equation}

The two initial states and two final states are coupled by monopole transitions, i.e., configuration interaction. The mixing parameter $t$ couples both configurations, and as $\Delta$ is the energy difference, the Hamiltonian is indicated with $t/\Delta$

\begin{equation}
H_{\text{MIX 1,12}} = \langle \text{3d}^{n} | t/\Delta | \text{3d}^{n+1}L \rangle \tag{15g}
\end{equation}

\begin{equation}
H_{\text{MIX 1,2}} = \langle 2p^5 \text{3d}^{n+1}L | t/\Delta | 2p^5 \text{3d}^{n+2}L \rangle \tag{15h}
\end{equation}

The spectrum is calculated by solving the eqs 15a-h. If a 3d$^{n+2}LL^\prime$ configuration is included, its energy is $2\Delta + U$, where $U$ is the correlation energy between two 3d electrons.\textsuperscript{125} The formal definition of $U$ is the energy difference one obtains when an electron is transferred from one metal site to another, i.e., a transition 3d$^8$ + 3d$^8$ $\rightarrow$ 3d$^{n-1}$ + 3d$^{n-1}$. The number of interactions of two 3d$^N$ configurations is one more than the number of interactions of 3d$^{n+1}$ plus 3d$^{n-1}$, implying that this energy difference is equal to the correlation energy between two 3d electrons.

In the final state of the X-ray absorption process, the configurations are 2p$^3$3d$^{n-1}$ and 2p$^5$3d$^{n+2}$L. A 2p electron is annihilated, and a 3d electron is created. Because the 3d electrons are relatively localized, this is an almost self-screened process. The consequence is that the relative ordering of the configurations does hardly change. To be precise: the energy difference between 2p$^3$3d$^{n-1}$ and 2p$^5$3d$^{n+2}$L is given as $\Delta + U - Q$, where $U$ is the 3d3d correlation energy and $Q$ the core hole potential, which identifies with the 2p3d correlation energy. From the systematic analysis of core-level photoemission spectra, it has been found that $Q$ is slightly larger than $U$. Typical values are $Q$ equal to 9 eV with $U$ equal to 7 or 8 eV. This is the reason that only small charge-transfer satellites are visible in X-ray absorption, in contrast to the large satellites in photoemission.\textsuperscript{29}

By analyzing the effects of charge transfer, it is found that (for systems with a positive value of $\Delta$) the main effects on the X-ray absorption spectral shape are (1) the contraction of the multiplet structures and (2) the formation of small satellites. Figure 12 shows the effect of the charge-transfer energy on divalent nickel. In the top spectrum, $\Delta = 10$ and the spectrum is essentially the ligand-field multiplet spectrum of a Ni$^{II}$ ion in its 3d$^8$ configuration. The bottom spectrum uses $\Delta = -10$, and now the ground state is almost a pure 3d$^9$L configuration. Looking for the trends in Figure 12, one nicely finds the increased contraction of the multiplet structure by going to lower values of $\Delta$. This is exactly what is observed in the series NiF$_2$, NiCl$_2$, and NiBr$_2$.\textsuperscript{87–89,115}

Going from Ni to Cu, the atomic parameters change very little, except the 2p spin–orbit coupling and the 2p binding energy. Therefore, the spectra of 3d$^N$ systems of different elements are all very similar and the bottom spectrum is also similar to Cu$^{I}$ systems. Therefore, one can also use the spectra with negative $\Delta$ values for Cu$^{II}$ systems, such as La$_2$L$_{12}$Cu$_{12}$O$_4$ and Cs$_2$KCuF$_6$. Figure 13 shows the comparison of the 2p X-ray absorption spectrum of these two compounds with charge-transfer multiplet calculations.\textsuperscript{63,64} It can be checked in Figure 12 that these calculations look similar to the calculations for Ni$^{II}$ systems with negative values of $\Delta$. For such systems with negative $\Delta$ values, it is important to carry out charge-transfer multiplet calculations as no good comparison with ligand-field multiplet spectra can be made.
IV. 1s X-ray Emission

Now the X-ray emission spectra will be discussed. The theory for X-ray emission spectra and resonant X-ray emission spectra has been described in, for example, the works of Åberg1,2,113 and Kotani.81,106 In this paper the models derived in these works will be used, starting with a simpler model.

A. 1s3p X-ray Emission in the Ligand-Field Multiplet Model

First the 1s3p X-ray emission spectral shape will be discussed, also known as K-fluorescence. With divalent manganese as an example, a scheme to interpret the experimental spectral shapes using the multiplet models as described for X-ray absorption will be developed step by step. The ground state of MnII has its five spin-up electrons filled. The five spin-down states are empty. It is first assumed that the core hole creation, for example, by an above-resonance X-ray excitation, does not modify the valence electron situation. The intermediate state has a 1s13d5 configuration and after the 1s3p decay the final state is 3p53d5.

The spectral shape consists of two structures separated by the 3p3d exchange interaction. This assignment is essentially the original model as used by Tsutsumi and co-workers.111,112 Starting from this model, the effects of the 3p and 3d spin–orbit coupling, the symmetry effects of the cubic crystal field, will step by step be included. In section V.A the model is extended to describe covalence effects as included with charge transfer and include the combined effects of off-resonance excitation and decay. Resonance effects will be discussed in section V.C.

Assuming a MnII ion, the atomic ground-state symmetry is 6S. In the 1s13d5 configuration, the total symmetry can be found by multiplying the 1s electron with the 6S symmetry of the 3d electrons. This gives either a 5S state for antiparallel alignment of the 1s and 3d electrons or 7S for parallel alignment. The dipole selection rules imply that transitions are possible from 5S to 5P and from 7S to 7P, with the energy difference between 5P and 7P given by the 3p3d exchange interaction. Things are a bit more complex in reality because more than one 5P configuration can be made from a 3p53d5 configuration. Writing out all symmetry combinations one finds three 5P states and one 7P state. Figure 14a shows the atomic multiplet spectrum for which the 3d and 3p spin–orbit couplings have all been set to zero. The overall intensities of the states are 7:5 for the 5P versus the 7P states. The main peak is the 7P state. The shoulder and the satellite are the 5P states, and the small peak at about −6487 eV is the third 5P state. The satellite can be related to the antiparallel aligned 3p and 3d electrons, while the shoulder and low-intensity state relate to orderings of the 3d electrons different from the ground state. In fact, the three 5P states are linear combinations of the three LS-like atomic states that are mixed by the strong 3p3d as well as 3d3d multiplet effects.

Figure 13. Results of theoretical simulations of the Cu 2p X-ray absorption spectra of Cs3KCuF6 (bottom) and La2Li1/2Cu1/2O4 (top), in comparison with the experimental spectra. (Reprinted with permission from ref 63. Copyright 1998 Elsevier Science.)

Figure 14. Theoretical 1s3p X-ray emission spectral shapes calculated with the ligand-field multiplet model. Bottom: (a) The ligand-field, 3d and 3p spin–orbit couplings have all been set to zero. Middle: The spin–orbit couplings are set to their atomic values. (solid, b) A cubic crystal field of 2.0 has been added. (dotted, c) A cubic crystal field of 4.0 eV has been added. (dashed, d) Top: Difference between b and c (×10).
Figure 14c shows the effects of the addition of a cubic crystal field of 2.0 eV. This is already a relatively large crystal field, and all oxides and halide systems have smaller crystal fields. It can be seen that compared to Figure 14b, most peaks shift a little bit. In particular, the $^3P$ states are modified while the $^7P$ states do still look very much like the atomic result. After broadening the sticks with the experimental and lifetime broadening, little changes are visible. This implies that 1s3p X-ray emission spectra are insensitive to the crystal-field effects, much less sensitive than, for example, 2p X-ray absorption. The positive aspect of this is that one can assume that the 1s3p X-ray emission spectra are virtually the same for all high-spin divalent manganese atoms. This finding is important for the use of the 1s3p X-ray emission channel for selective X-ray absorption measurements as will be discussed in section VII. It is noted that all other crystal-field effects in systems such as oxides will have no effect at all on the spectral shape (within the ligand-field multiplet model) as long as the spin state stays the same. Things are different for low-spin Mn$^{II}$ compounds. Figure 14d shows the effect of a cubic crystal field of 4.0 eV. A completely different spectrum is found. The reason is that the ground-state symmetry has changed from $^6A_1$ to $^2T_2$. Thus, only one unpaired 3d electron remains, leading to a very small 3p3d exchange splitting and essentially no satellite. It is clear that 1s3p X-ray emission will immediately tell if a system is in its high-spin or low-spin state.

Similar to 2p X-ray absorption, 1s3p X-ray emission is sensitive to the valence of the metal. Mn$^{II}$ has a 3d$^5$ ground state and Mn$^{III}$ a 3d$^4$ ground state. This obviously leads to a different spectral shape in the experiments. Figure 15 shows an example of the variations in the manganese 1s3p X-ray emission spectral shapes. Each spectrum can be simulated with a multiplet calculation leading to the determination of the valence. It can be seen that there is a clear shift between the spectra.

These chemical shifts have been studied in detail by Bergmann and co-workers, who established that it was more accurate to use the center of gravity of the 1s3p X-ray emission spectral shape as an energy indicator. The nature of the Mn oxidation states involved in the oxygen-evolving complex in photosystem II has been studied with this method. The measurements have been made on the dark-adapted S$_1$ state and on the hydroquinone-reduced state. The results are compatible with models involving conversion of Mn$^{II/IV}_{2}$Mn$^{II/IV}_{2}$ to Mn$^{II/IV}_{2}$Mn$^{II/IV}_{2}$ clusters.

B. 1s3p X-ray Emission in the Charge-Transfer Multiplet Model

In the previous sections the approximation that one can calculate the 1s3p X-ray emission spectral shape from a model using the following two transitions was used, where the excitation step is not used explicitly in the results

$$3d^5 \rightarrow 1s^1 3d^6 + e 1s^1 3d^6 \rightarrow 3p^5 3d^6$$

In Mn$^{II}$, this model gives a good account of the spectral shape. If one looks at other systems though, an agreement that is not as good is found. The main reason for this is that in the 1s excitation step major screening or charge-transfer effects occur. Essentially one is removing a core electron, implying a core charge that has increased by one. This pulls down the valence 3d electrons by the core hole potential. Because the 3d electrons are pulled down in a larger energy than the 4s and 4p electrons, the intermediate-state configurations will be different from the ground-state configurations. Essentially one has to subtract the core hole potential Q from the ground-state energy positions as used in the charge-transfer model. Below the transitions are given for two configurations

$$3d^5 + 3d^6_L \rightarrow 1s^1 3d^6 + 1s^1 3d^6_L$$

$$1s^1 3d^6 + 1s^1 3d^6_L (lowest) \rightarrow 3p^5 3d^6 + 3p^5 3d^6_L$$

The lowest two intermediate states are selected, and the 1s3p X-ray emission spectrum is calculated for these states, which implies that one assumed the intermediate states to relax to their lowest configuration(s). Two states are used, because the lowest state is split by the 1s3d exchange interaction. This ‘relaxed’ model has been used in the calculations of the 1s3p X-ray emission spectra of divalent nickel compounds. Using an intermediate-state configuration, 1s$^3$3d$^6 + 1s^3$3d$^6_L + 1s^3$3d$^{10}$LL$^*$. The charge-transfer values for NiBr$_2$ and NiF$_2$ are, respectively, 4.3 and 0.3 eV, and with a core hole potential of 7.5 eV and a correlation energy U of 7.3 eV, this gives that the lowest energy is the 1s$^3$3d$^6_L$ configuration. For NiF$_2$, the 1s$^3$3d$^6$ configuration has an energy of 3.2 eV and the 1s$^3$3d$^{10}$LL$^*$ configuration of 4.1 eV. In the case of NiBr$_2$, these values are, respectively, 7.2 eV and 0.1 eV.

The ‘relaxed’ charge-transfer model used is not necessarily the correct model. Another approach is to assume that the intermediate states do not relax at all. In this section this approximation will be
is a negative number and the lowest energy configuration larger than the charge-transfer energy, this is a electron annihilates a proton and is captured in the spectrum states. In the K-capture process, the 1s calculated by adding the 1s3p spectra of the 1s XPS atom as a continuum electron, and the spectrum is scheme as outlined above. The 1s electron leaves the for MnO.6 The X-ray excitation process follows the resonance X-ray excitation with K-capture excitation. Glatzel and co-workers compared the usual above the 1s3p X-ray emission spectral shapes will be explicitly used.

1. K Capture 1s3p X-ray Emission

The effects of the excitation process can be studied by using two different excitation processes. Recently Glatzel and co-workers compared the usual above resonance X-ray excitation with K-capture excitation for MnO.6 The X-ray excitation process follows the scheme as outlined above. The 1s electron leaves the atom as a continuum electron, and the spectrum is calculated by adding the 1s3p spectra of the 1s XPS spectrum states. In the K-capture process, the 1s electron annihilates a proton and is captured in the core.6 The calculation is the same as that for X-ray excitation as given above. The difference is the ordering of the configurations. As indicated in Figure 16, the energy difference between 1s13d5 and 1s13d6 is equal to that in the ground state, being Δ. The K-capture spectrum is sharper, and the satellite structure is found at a lower energy, which is a consequence of additional states in the X-ray excited spectrum. The simulated spectra correspond nicely with the experimental results.6

2. Temperature- and Pressure-Dependent 1s3p X-ray Emission

1s3p X-ray emission spectra involve hard X-rays for both excitation and decay. Because only hard X-rays are involved in the experiment, one has a large flexibility in the experimental setup as well as sample environment. This makes it relatively straightforward to carry out the 1s3p X-ray emission experiment in situ, for example, at high-temperature, high-pressure, etc.33

Tyson and co-workers91,114 measured a series of manganese perovskites using 1s3p X-ray emission to determine the valences of Mn in these systems. In particular, they measured the temperature dependence of the 1s3p X-ray emission spectral shape. The low-temperature spectrum of La₅Ca₅MnO₃ has more weight close to the center of gravity compared with the room temperature spectrum. From Figure 15 (and more clearly Figure 32b), it can be concluded that spectral weight closer to the center of gravity indicates a smaller 3p3d exchange splitting, implying less unpaired 3d electrons. The reason for the decrease in unpaired 3d electrons can be either a valence change or a spin transition. In the case of La₅Ca₅MnO₃, the decrease of unpaired 3d-electrons is attributed to a valence increase.91 Rueff and co-workers97,98 used the 1s3p X-ray emission spectral shape for the analysis of pressure-dependent spectra of Fe and FeS. The structural and magnetic transition between the magnetic (bcc) and the nonmagnetic (hcp) iron phases has been observed from the shift of intensity toward the center of gravity.

C. 1s2p X-ray Emission

The situation of the 1s2p or Kα X-ray emission spectra is analogous to the 1s3p X-ray emission spectra. This situation is alike the comparison between 2p X-ray absorption and 3p X-ray absorption. The calculation in the various models discussed above is exactly the same, the only difference being the different parameters of the 2p instead of the 3p core electrons. The 2p spin–orbit coupling is much larger than the 3p spin–orbit coupling, typical values being, respectively, 10 and 1 eV. This implies that the spin–orbit-split states are clearly visible in the experimental spectral shapes. In contrast, the 2p3d exchange interaction is much smaller than the 3p3d exchange. This implies that the satellites visible in the 1s3p X-ray emission spectra will only be shoulders in the case of 1s2p X-ray emission.

Figure 17 shows the theoretical 1s2p X-ray emission spectra of FeII, and Figure 18 shows the corresponding 1s3p X-ray emission spectra. The calculations are performed with the ligand-field multiplet approach as discussed in section IV.A. The spectra have been divided into spin-up and spin-down, and this aspect will be discussed in the next section. The
1s3p X-ray emission spectrum is split into a main peak at +5 eV, where 0 eV is the average 1s3p excitation energy. A satellite is visible at about -12 eV, the energy difference being the 3p3d exchange splitting. The 1s2p X-ray emission spectrum also has its main peak at +5 eV and a satellite at about -9 eV. This general spectral shape thus looks similar to the 1s3p case, but the origin of the splitting is different, 2p-spin–orbit, respectively, and 3p3d exchange. This assignment is confirmed if one looks at the top spectra that relate to low-spin Fe⁺ systems. Low-spin Fe⁺ has no unpaired 3d electrons (i.e., a 1A1 ground state); hence, no exchange splitting and the satellite is absent. Only some low-energy shoulders are visible due to other (multiplet) effects. In the case of the 1s2p X-ray emission spectrum, not much has changed for the low-spin situation. The 2p spin–orbit coupling is the same, and the satellite maintains a similar structure and intensity.

The 1s2p X-ray emission spectrum is a few times more intense than the 1s3p X-ray emission spectrum, and one might expect more studies using the 1s2p channel. However, the chemical sensitivity of the 3p3d exchange interaction makes the 1s3p X-ray emission spectrum more useful for determining the spin state and valence.

D. 1s2p Resonant X-ray Emission

In this section I focus on the effects that occur if one excites at resonance. I will go deeper into this issue when the soft X-ray 2p resonances, where interference effects are more important, are discussed. This section deals with resonance effects at the K edges. It will be shown that the study of 1s2p resonant X-ray emission sheds light on the nature of the intermediate states, in other words the final states of the X-ray absorption process.

Figure 19 shows the 1s2p resonant X-ray emission spectra of Fe₂O₃ excited at resonance. Spectra a, b, and c have been measured at the positions of the K edge as indicated in Figure 20. The spectrum is normalized so that the measured absorption coefficients for photon energies immediately below and well above the absorption edge are the same as the theoretical values. Several weak preedge peaks are clearly observed. The first two preedge peaks, located...
at 7113.4 and 7114.8 eV, are assigned to the quadrupole transitions from the Fe 1s orbital to the crystal-field split t_{2g} and e_{g} orbitals. These spectra have been measured by Caliebe and co-workers at NSLS beamline X21 with an overall resolution of 0.45 eV. With this high experimental resolution, 1s2p X-ray emission spectra are measured well.

Recently, Dräger and co-workers performed similar experiments on single crystals of MnO. The manganese 1s preedge structure is different for measurements with a (100) and (110) orientation of the rock salt crystal structure. The (100) spectrum gives transitions to the empty e_{g} states and the (110) spectrum to the empty t_{2g} states. The resonant 1s3p X-ray emission spectra have been used to disentangle the spin-polarization of the X-ray absorption spectrum.46

The 1s2p resonant X-ray emission spectra can be calculated with the charge-transfer multiplet model as described for X-ray absorption above. Charge-transfer multiplet calculations have been carried out for the 3d^{5} ground state, the 1s^{3}3d^{6} intermediate states (\phi_{j}), and the 2p^{3}3d^{6} final states, including the quadrupole excitation (Q) and the dipole decay (D)

\[
d\frac{d^{2}\sigma}{d\Omega d\omega} \propto \sum_{\phi_{j} Q} \left( \begin{array}{c}
2p^{5}3d^{6}\rangle\langle 1s^{3}3d^{6}\rangle\langle 1s^{3}3d^{6}\rangle Q\langle 3d^{5}j\rangle
\end{array} \right)^{2}.
\]

Three configurations 3d^{6}, 3d^{4}L, and 3d^{6}LL' have been used for the ground state, and the corresponding three configurations have been used for the intermediate and final states. The result of the calculations is indicated in Figure 19 as the solid lines. For these calculations, the dipole transitions to 1s^{3}3d^{6}4p^{1} states have been included also but they do not significantly affect the calculated spectral shapes.23

Why is this resonant experiment so interesting? One could say that the only result of the experiment is a 1s2p resonant X-ray emission spectrum that could also be measured directly with 2p X-ray absorption. There are at least two interesting consequences of this experiment. First, it adds additional proof as to the quadrupole nature of the prepeaks in the K edge of Fe_{2}O_{3}. Second, it makes it possible to measure a spectrum similar to 2p X-ray absorption spectra. Apart from dipole X-ray emission, there can be quadrupole X-ray emission directly from the 3d states.

Figure 22 shows a comparison of a K/\beta, crossover, and valence band X-ray emission spectrum of MnO. The intensity is given on a logarithmic scale.

**Figure 21.** X-ray emission decay to a 1s core hole in MnO. Indicated are, respectively, 1s2p (K/\alpha), 1s3p (K/\beta_{1}), and 1s-valence band (K/\beta_{2,5}) X-ray emission.

**Figure 22.** 1s3p, crossover, and valence band X-ray emission spectrum of MnO. The intensity is given on a logarithmic scale.

and valence band X-ray emission spectra of MnO.8

As indicated in the figure, there is a K/\beta peak related to manganese 3p core holes, the crossover peak related to oxygen 2s core holes, and the valence band related to oxygen 2p holes. Figure 23 shows a series of valence band X-ray emission spectra for manganese oxides. The bottom two spectra are manganese metal and MnF_{2}. The energy of the valence band peak in the oxides shifts approximately 1 eV per increment in oxidation state. This is indicated in the inset.

The intensities of the crossover peaks change significantly in the various oxides indicated in Figure 24. The integrated intensity of the crossover peak can be normalized by the main K/\beta region, correcting for the number of oxygen atoms per Mn. Assuming that the integrated intensity per Mn of the main K/\beta region
is chemically invariant, this procedure yields the relative crossover transition probability per Mn-O pair. The inset of Figure 24 shows that the bond length varies exponentially with distance, and it can be concluded that the intensity of the crossover peak can be used as a tool to determine Mn-O distances to within 0.1 Å.  

V. 2p X-ray Emission

The 2p core levels of the 3d transition metals are positioned in the soft X-ray range between 400 and 1000 eV. As discussed in section III, the 2p X-ray absorption spectra are dominated by multiplet effects and do show a complex multiplet spectral shape. This makes 2p X-ray emission ideally suitable for resonance studies. Therefore, this begins with a discussion of the resonant 2p X-ray emission spectral shapes. Both 2p3s and 2p3d resonant X-ray emission will be discussed.

If the core hole is created with an energy close to the 2p absorption edge, the X-ray absorption and X-ray emission processes do occur coherently and the overall 2p3d process (of a 3d5 ground state) is described with the Kramers-Heisenberg formula

\[ I(\omega,\omega') \sim \sum_{2p3d^6} \left\langle 3d^5|\hat{e} \cdot \hat{r}|2p^53d^6\right\rangle \left\langle 2p^53d^6|\hat{e} \cdot \hat{r}|3d^5\right\rangle E_{2p3d^6} - E_{3d^6} - \hbar \omega - \hbar \omega' \right \rangle^2 \]  

(17)

This formula forms the basis of all resonant X-ray processes. The intensity \( I(\omega,\omega') \) is given as a function of the excitation \( \omega \) and the emission \( \omega' \) energies. The initial state \( 3d^5 \) is excited to an intermediate state \( 2p^53d^6 \) with the dipole operator \( \hat{e} \cdot \hat{r} \), and the second dipole operator \( \hat{e} \cdot \hat{r} \) describes the decay to the final state \( 3d^5 \). The denominator contains the binding energy of the intermediate state and its lifetime broadening. A resonance occurs if the excitation energy is equal to the binding energy of the intermediate state. Looking at the MnO 2p X-ray absorption spectrum of Figure 11, each multiplet line can give rise to a different resonant 2p3d X-ray emission spectral shape.

The general spectral landscape can be viewed as a two-dimensional space with axis \( \omega \) and \( \omega' \). Figure 26 shows a contour plot of the 2p3d resonant X-ray emission spectrum of NiII using a crystal field of 1.12 eV to simulate NiO. The darkest area has the highest intensity. The horizontal axis shows the X-ray excitation energy. The main peak of the 2p X-ray absorption spectrum of NiO has an energy of 855.7 eV with a shoulder at 857.5 eV. The vertical axis shows the X-ray energy loss, that is the energy of 0.0 eV means that the 2p3d decay energy is equal to the 2p3d excitation energy, in other words this refers to resonant elastic scattering. There is a large peak visible with its peak position at (855.7 eV, 0.0 eV). There is a second peak at an energy loss of 1.1 eV. This peak relates to a ligand-field excitation from the \( 3A_2 \) ground state to the \( 3T_2 \) excited state. A third peak is visible at approximately −2.0 eV.

A number of cross sections can be made. This paper focuses on the (resonant) X-ray emission spectral
shape excited with a fixed energy. This will be indicated as $I^{\omega}_{XES}(\omega')$. In Figure 25, this relates to

$$I^{\omega}_{XES}(\omega') \sim \left| \sum_{2p^33d^1} \frac{(3s^13d^1\hat{e} \cdot r)(2p^53d^1\hat{e} \cdot r)(2p^53d^1\hat{e} \cdot r)(3d^0)}{E_{2p^33d^1} - E_{3d^0} - \hbar \omega - i\Gamma_{2p}} \right|^2 \text{(18)}$$

This calculation can almost be carried out 'by hand'. Starting from the situation in CaF$_2$ with all bands completely full, one has the advantage of strong restrictions on the possible symmetry states. Ligand-field multiplet calculations have been performed for the 3d$^0$ initial state, the 2p$^3$3d$^1$ intermediate states, and the 3s$^1$3d$^1$ final states in cubic symmetry. The 3d$^0$ initial state consists of only one state with $^1A_1$ symmetry. The only 2p$^3$3d$^1$ intermediate states that can be reached in X-ray absorption must have $T_1$ symmetry, and as there will be seven of those states. The 3s$^1$3d$^1$ final states are split by only two interactions, the 3s3d exchange and the cubic crystal field. This gives a total of four peaks in the final state. The complete calculation is then the transition of one initial state via seven intermediate states to four final states. The results of these seven absorption matrix elements and 28 (in fact 49 due to degeneracies) emission matrix elements are fed into the Kramers–Heisenberg formula.

Figure 27 gives the resulting resonant 2p$^3$s X-ray emission spectral shapes. One can observe that in all comparisons of interference-on (solid line) and interference-off (dashed), the integrated intensities of the solid and dashed line are equivalent or in fact identical as the integrated intensity is conserved by

A. 2p$^3$s Resonant X-ray Emission

Before returning to the 2p$^3$ resonant X-ray emission spectra, the 2p$^3$s resonant X-ray emission spectra will be discussed first as the 2p$^3$s case gives a good opportunity to describe essentially all peaks with a simple model. The calculation of the 2p$^3$s resonant X-ray emission spectra of CaF$_2$ will be followed. The X-ray absorption spectrum of CaF$_2$ has been given in Figure 10. In resonant 2p$^3$s X-ray emission, one is exciting at all seven peaks in the absorption spectrum and measures the 2p$^3$s X-ray emission spectral shape, as measured by Rubensson and co-workers.\textsuperscript{95,96} The 2s2p inelastic X-ray scattering cross section is dominated by resonant scattering via the 2p$^3$3d$^1$ intermediate states. It has been shown that one can reduce the calculation to the transitions of 3d$^0$, via 2p$^3$3d$^1$, to 3s$^1$3d$^1$ states. The effects of charge transfer are small and can be neglected. Both the X-ray absorption and X-ray emission steps essentially conserve the local charge, and it has been shown that in those experimental conditions, ionic systems such as CaF$_2$ can be described in close detail by the ligand-field approximation. One has to fill in the X-ray absorption and X-ray emission steps in the Kramers–Heisenberg formula

$$I(\omega,\omega') \sim \left| \sum_{2p^33d^1} \frac{(3s^13d^1\hat{e} \cdot r)(2p^53d^1\hat{e} \cdot r)(2p^53d^1\hat{e} \cdot r)(3d^0)}{E_{2p^33d^1} - E_{3d^0} - \hbar \omega - i\Gamma_{2p}} \right|^2 \text{(18)}$$

This calculation can almost be carried out 'by hand'. Starting from the situation in CaF$_2$ with all bands completely full, one has the advantage of strong restrictions on the possible symmetry states. Ligand-field multiplet calculations have been performed for the 3d$^0$ initial state, the 2p$^3$3d$^1$ intermediate states, and the 3s$^1$3d$^1$ final states in cubic symmetry. The 3d$^0$ initial state consists of only one state with $^1A_1$ symmetry. The only 2p$^3$3d$^1$ intermediate states that can be reached in X-ray absorption must have $T_1$ symmetry, and as there will be seven of those states. The 3s$^1$3d$^1$ final states are split by only two interactions, the 3s3d exchange and the cubic crystal field. This gives a total of four peaks in the final state. The complete calculation is then the transition of one initial state via seven intermediate states to four final states. The results of these seven absorption matrix elements and 28 (in fact 49 due to degeneracies) emission matrix elements are fed into the Kramers–Heisenberg formula and this gives Figure 26 as its result.
a sum rule. Relatively large interference effects can be seen for the spectra excited at 347.5 and 348.1 eV. These two energies relate to weak excitations; hence, the decay spectrum is dominated by the Lorentzian tails of the neighbors. That is, interference effects are largest if two channels have a comparable effective strength at a certain energy. The experimental results are reproduced with these calculations.

A topic not discussed in this paper is the consequences of intermediate-state decay/relaxation, also known as postcollision interactions, as observed in the experimental spectra. These decay channels do give rise to nonresonant X-ray emission. Far above the edge the situation is clear and these nonresonant channels are the normal fluorescence lines at constant energy, but the nonresonant channels close to and even at resonance present a theoretical challenge as they can (and will) be different both from resonant X-ray emission and also from the normal nonresonant channels. To shed light on this situation, one has to understand in great detail what happens exactly in the various relaxation and decay channels, both elastic as inelastic. In solids this is a dramatically complex situation and little is known quantitatively. The situation is a bit better known in atomic spectra, and the interested reader is referred to those papers, for example, the recent review by Gel'mukhanov and Agren.

B. 2p3d Resonant X-ray Emission

The first high-resolution 2p3d resonant X-ray emission experiments have been carried out by the group of Nordgren.

Figure 26. Plot of the two-dimensional resonant landscape of CaF₂. The excitation energy is given on the x axis; the final-state energy is given on the y axis. (Reprinted from ref 31. Copyright 1996 American Physical Society.)

Figure 27. Cross sections through Figure 22 at the excitation energies as indicated on the right. The dotted lines give the decay of only the excited state at precisely the energy indicated. The dashed lines include the Lorentzian tails of the neighboring states, and the solid lines include interference effects. (Reprinted with permission from ref 31. Copyright 1996 American Physical Society.)
could be nicely explained with ligand-field multiplet calculations, while the other oxides needed the inclusion of charge-transfer effects. The calculations confirm that it is crucial to include the correct angle between incoming and outgoing X-rays, i.e., the correct combinations of X-ray polarization. The NiO and CoO spectra excited at the charge-transfer satellites of the 2p X-ray absorption reveal large satellites in the resonant X-ray emission. These satellites are positioned at a similar X-ray energy as the off-resonance 2p3d X-ray emission, but the charge-transfer multiplet calculations show that they are caused by resonant satellites related to a final state with a ligand hole. The transition can be envisaged as 3d10 → 2p3d5 + L → 3d5+1L, where the initial and final states are simplified to their main configuration, i.e., one observes the charge-transfer excitation. The situation of the 3d4f resonant X-ray emission spectra of the rare-earth metals is very interesting. One can beautifully observe the resonances of the charge-transfer satellites. In addition, one observes ff transitions from which one can determine the crystal-field values of the 4f electrons.

2. Coster–Kronig Transitions

Hague and co-workers recently showed that in the case of resonant X-ray emission of TiCl4 molecules, it is not enough to include only the direct resonances as described with eq 18. In addition, the three-step transition via a Coster–Kronig decay channel must be added to describe the observed spectral shapes.

\[
I(\omega, \omega') \sim \sum_{X_1X_2} \frac{(3d^0 + 3d^1L \hat{e} \cdot \hat{r}|X_2)(X_2|H_{CK}|X_2)(X_2|\hat{e} \cdot \hat{r}|3d^0 + 3d^1L)}{(E_{X_1} - E_3d^0 - \hbar \omega - iI\gamma_2 p)(E_{X_2} - E_{3p} - \hbar \omega - iI\gamma_2 p)^2}
\]

Equation 19 shows the Kramers–Heisenberg formula for this three-step pathway. The initial and final states are 3d0 + 3d1L. The intermediate states X1 and X2 have a configuration 2p3d1 + 2p3d2L. In ref 59, transitions to the continuum have also been included. It was shown that the experimental spectral shapes could only be described correctly with the inclusion of both the Coster–Kronig channel and the explicit inclusion of continuum states.

3. Spin-Flip Transitions

Above it was shown that resonant 2p3d X-ray emission can give information on dd excitations and charge-transfer excitations. Also, other low-energy excitations can be studied, for example, it has been shown that spin-flip transitions can be observed in resonant 2p3d and 3p3d X-ray emission of nickel and copper oxides.
spectra at the 2p X-ray absorption spectrum of NiO. This figure is related to Figure 25 discussed above. The resonant elastic peak of $^3A_2$ symmetry is visible at 0.0 eV, and the dd transitions to the $^3T_2$, $^3T_1$, and $^1E$ states are visible at energies of 1.1 eV and at about 2.0 eV energy loss. However, some additional peaks are visible at low-energy loss. For example, a peak is visible at about 0.25 eV. This peak can be assigned to a spin-flip transition in which a Ni$^{II}$ ion flips its spin state from +1.0 to -1.0 (or reversed). The consequence of this spin flip is that the antiferromagnetic neighbors now see an apparent ferromagnetic neighbor and the energy involved is the energy loss observed in resonant X-ray emission. The spin-flip peak is highest at an excitation energy of 858 eV that is at the shoulder of the 2p X-ray absorption spectral shape. The reason is that this shoulder that is at the shoulder of the 2p X-ray absorption is highest at an excitation energy of 858 eV loss observed in resonant X-ray emission. The spin-flip peak is highest at an excitation energy of 858 eV loss observed in resonant X-ray emission. The spin-flip peak is highest at an excitation energy of 858 eV loss observed in resonant X-ray emission. The spin-flip peak is highest at an excitation energy of 858 eV loss observed in resonant X-ray emission. The spin-flip peak is highest at an excitation energy of 858 eV loss observed in resonant X-ray emission. The spin-flip peak is highest at an excitation energy of 858 eV loss observed in resonant X-ray emission. The spin-flip peak is highest at an excitation energy of 858 eV loss observed in resonant X-ray emission.

It is good to note that in the literature two completely distinct transitions are called spin flip. There is the spin flip as described above that is related to the transition of a $ms = -1$ state to a ms = +1 state. The other usage of the term spin flip is given to transitions in which the spin ‘flips’ from, for example, a sextet state to a quartet state. These types of ‘spin flip’ can be seen in all but the elastic transition in Figure 28. The total spin state has been modified in such a spin-flip transition. In my opinion it is better to refer to such transitions simply as dd transitions.

The measurement of spin-flip transitions is important for the study of the antiferromagnetic coupling in transition-metal oxides. There is, however, an experimental complication which is that the overall resolution of the experiment should preferably be on the order of 0.2 eV. This is at the edge of the present technology and still suffers from low intensities. A first measurement has been performed by Kuijper and co-workers using the 3p3d resonance instead of 2p3d. In the future, more studies of the spin-flip effect are expected to yield important new information on the magnetic couplings in transition-metal oxides and other transition-metal systems.

From the discussion of the 2p3d resonant inelastic X-ray scattering, it is concluded that there are many aspects that must be included for a correct description of the spectral shapes. It depends essentially on the resolution (and system) used and what excitations and pathways must be included. In principle, one can extend the model further by adding other configurations and pathways. Important excitations one can observe are charge-transfer transitions, dd transitions, and spin-flip transitions. Excitations into the continuum and Coster–Kronig three-step pathways could until now only be established in molecular systems. This must be related to a difference in electronic structures between molecular systems and solids.

## VI. X-ray Magnetic Circular Dichroism

X-ray magnetic circular dichroism (X-MCD) is an important phenomenon in both X-ray absorption and X-ray emission. The magnetic structure of a system is studied by making use of circular or linear polarized X-rays. In the last 10 years many papers have been published on X-MCD. In this review, some general features of X-MCD are discussed. A recent overview is given by Duda. The focus is on X-ray emission MCD, and in line with the historic development, X-ray absorbance MCD is introduced first.

### A. MCD in X-ray Absorption

The MCD effect in X-ray absorption is defined as the difference in absorption between left- and right-polarized X-rays. A nonzero MCD effect is observed only in magnetic systems (the natural dichroism effects are neglected). The MCD effect has a maximum if the polarization vector of the X-ray is parallel or antiparallel to the magnetization vector of the system.

The MCD effect in X-ray absorption has been measured for the first time by Schütz and co-workers. They showed that the absorption cross section is different for left- and right-polarized X-rays. The difference between the left- and right-polarized X-rays was shown to be proportional to the spin-polarized density of states. Using the proportionality between X-ray absorption (I$_{XAS}$) and the density of state ($\rho$) as the starting point, one obtains

$$I_{MCD} \equiv \frac{I_{XAS}^L - I_{XAS}^R}{I_{XAS}^L + I_{XAS}^R} = \frac{\rho_+ - \rho_-}{\rho_+ + \rho_-}$$

where $I^L$ denotes left-polarized X-rays and $I^R$ denotes right-polarized X-rays. $\rho_+$ and $\rho_-$ relate to, respectively, spin-up and spin-down density of states. The proportionality factor $F_+$ is the Fano factor. The original paper used the iron K edge as an example and did find a small effect, in other words, did find a Fano factor of approximately 0.01. It was later shown that this small MCD effect was particular to the use of a 1s core level and was related to the absence of a core hole spin–orbit coupling. For details on many aspects of this effect, the reader is referred to the book Spin–orbit influenced spectroscopies of magnetic solids.

If a core level has spin–orbit coupling, the MCD effect in X-ray absorption is much larger. If one neglects the overlap of the core and valence wave functions and uses single-electron transition matrix elements, one can simply explain the size of the MCD effect. For example, p $\rightarrow$ d transitions have relative magnitudes for parallel and antiparallel alignments at the 2p$_{3/2}$ edge of P$_{3/2}$ = 5 and A$_{3/2}$ = 3, respectively. The related numbers at the 2p$_{1/2}$ edge are, respectively, P$_{1/2}$ = 1 and A$_{1/2}$ = 3. This directly yields the relative intensity of the 2p$_{3/2}$ and 2p$_{1/2}$ edges of 8:4. The MCD effect is given as $(P - A)/(P + A)$, leading to $+1/4$ for the L$_3$ edge and $-1/2$ for the L$_2$ edge.

An important development in the use of X-MCD was the development of sum rules by Thole and co-workers. It was shown that the integral of the X-MCD signal could be related to the ground-state expectation value of the orbital moment ($L_z$). A second sum rule was postulated relating the weighted integral of the L$_3$ edge plus the L$_2$ edge to an effective
spin moment. Many papers deal with the validity, derivation, and experimental complications of the sum rules. The reader is referred to the Theo Thole memorial issue of the Journal of Electron Spectroscopy.\textsuperscript{34}

Recently, the X-MCD signal at the L\textsubscript{2,3} edges has been used as a probe signal for microscopy using a photoemission electron microscope (PEEM).\textsuperscript{85,100,102} In addition, the MCD signal has been used for nanosecond time-resolved studies by the group of Alain Fontaine.\textsuperscript{79}

1. MLD in X-ray Absorption

Magnetic linear dichroism (MLD) is essentially the angular dependence of the absorption cross section. This is an often used technique in X-ray absorption, in particular to study directional variations in the electron density, used, for example, for surfaces and single crystals and to disentangle dipole and quadrupole contributions.\textsuperscript{101} In 1985, Thole and co-workers\textsuperscript{109} predicted a strong magnetic effect on the polarization dependence, an effect that became studied as X-MLD in the last 15 years.

In contrast to X-MCD that probes the magnetic direction, X-MLD only probes the orientation of the magnetic moment, in other words it probes the squared expectation value of the magnetic moment. This automatically implies that X-MLD can intrinsically not make a distinction between magnetic effects and other effects that cause a directional variation of the absorption cross section. To study a magnetic effect with X-MLD, one always has to make sure that the effect is indeed magnetic in origin, for example, by a measurement of the same system without being magnetically ordered. The same reasoning applies to MLD in X-ray emission.

B. MCD in X-ray Emission

In 1991, Strange and co-workers\textsuperscript{104} pointed out that dichroism in X-ray emission spectra can be studied with incident photons that are circularly polarized. It was argued that such an experiment would probe the spin-polarization of the valence band. These experiments are discussed below, where soft X-ray and hard X-ray experiments will be differentiated, i.e., decay to metal 2p and metal 1s core holes, respectively.

If one uses circularly polarized X-rays for the excitation process, naturally this has consequences for the resonant X-ray emission spectra. The basic idea is that the use of circular polarization for the 2p core excitation will create an imbalance between 2p spin-up and spin-down core holes (with respect to the magnetization of the 3d valence electrons). This imbalance implies that detecting the decay of the 3d valence band electrons to the polarized 2p core hole will create an imbalance in the spectral shape that is proportional to the spin polarization of the conduction band. With this starting point in mind, many experiments have been carried out.\textsuperscript{9,22,58,68} It turned out that the situation in the soft X-ray range is complex because of both experimental and theoretical complications.

Figure 30. Comparison of the calculated 2p3d X-ray emission spectral shape (—) with the 2p\textsubscript{3/2}3d experimental results (····). (Reprinted with permission from ref. 42. Copyright 1997 American Physical Society.)

On the level of a single-particle analysis, already the situation is complex. The single-particle analysis assumes that the MCD effect can be described by the p ← d matrix elements only. This approach can be found in the works of Erskine and Stern,\textsuperscript{49} Stöhr and Wu,\textsuperscript{103} Jo and co-workers,\textsuperscript{65–67} and Kuiper.\textsuperscript{76} In the last reference the argument was used that spin is not a constant of motion in the 2p core hole state. Because of the large core hole spin–orbit coupling, the spin of the core hole will not remain aligned with the spin of the photoelectron. This has direct consequences on the nonresonant and resonant X-ray emission MCD effects.\textsuperscript{76}

An important experimental complication is the self-absorption-caused saturation effects. A high concentration of the element that is absorbing the X-rays implies that an emitted X-ray emission signal can be re-absorbed before leaving the sample to be measured at the detector. Saturation effects affect the X-ray emission spectral shapes, including the MCD effects. In principle, they can be corrected for, but in the case of concentrated systems, this is a nontrivial exercise.\textsuperscript{10} Braicovich and co-workers recently showed that by using the 2p3s X-ray emission channel, self-absorption effects can be excluded.\textsuperscript{11} This paper used the fact that there is an angular dependence of the fluorescence and of the MCD effect therein.\textsuperscript{42,108}

In the hard X-ray range, most of the experimental complications disappear. However, it is known that the K-edge MCD effect is very small.\textsuperscript{49} There has been a series of studies on the MCD effect of the rare-earth L\textsubscript{edges}. Figure 30 shows the MCD effect in the 2p\textsubscript{3/2}3d X-ray emission spectrum of Gd metal.\textsuperscript{5,74,75} By taking care of the multiplet interactions and the
angles between incident X-rays, emitted X-rays, and magnetic field, one can simulate the experimental spectra as shown in Figure 30.

1. MLD in X-ray Emission

In analogy with absorption magnetic linear dichroism (MLD), the X-ray emission MLD effect is the angular dependence of the X-ray emission cross section with respect to the magnetization vector. Figure 31 shows the magnetic linear dichroism effect in the Yb 2p1/2-4d X-ray emission spectrum of Yb2Fe12O19.40 X-ray emission spectra were recorded at 30° and 70°. (top) 2p1/2-4d X-ray emission spectral shape as a function of X-ray emission energy at detection angles of 30° (---) and 70° (---). (bottom) Difference spectrum (70° -- 30°). (Reprinted with permission from ref 40. Copyright 2000 American Physical Society.)

**Figure 31.** (top) 2p1/2-4d X-ray emission spectral shape as a function of X-ray emission energy at detection angles of 30° (---) and 70° (---). (bottom) Difference spectrum (70° -- 30°). (Reprinted with permission from ref 40. Copyright 2000 American Physical Society.)

It has been eluded already in section III that 1s2p and 1s3p X-ray emission channels will conserve their spin state, the two 1s intermediate states will be spherically symmetric, because only core levels are involved in the X-ray emission process itself. This implies a zero integrated intensity over the MLD effect. The same is true for the MCD effect, as the electron is excited from a core state to a continuum state some 100 eV above the edge, where no significant MCD effect is expected in the absorption. While the integrated intensity of the MCD and emission MLD effects is zero, their amplitude is proportional to the 4f magnetization, because it is the 4d4f exchange interaction which gives rise to the appearance of the dichroism signal. It therefore shares this sensitivity with the 3d and 4d absorption MCD and absorption MLD spectra of the rare-earth metals. It can be shown that the size of the emission MLD effect appears as a property that is sensitive to the 4f magnetic moments of the rare-earth metals. This technique is therefore complementary to absorption MCD spectroscopies at the rare-earth 3d and 4d edges, which have to be performed in the soft X-ray regime. This technique can obviously be extended to 3d transition-metal systems where the 1s2p and 1s3p X-ray emission channels will have a MLD effect that is, in this case, sensitive to the 3d magnetic moment. Magnetic linear dichroism in X-ray emission is likely to become a useful new technique in the study of magnetic materials, since it circumvents the intrinsic complications of soft X-ray spectroscopies such as a high-vacuum environment and electron detection. Furthermore, the use of hard X-rays implies that the technique is a bulk-sensitive probe and in situ experiments will be possible.

E. Spin-Polarized 1s2p and 1s3p X-ray Emission

Spin-polarized 1s2p X-ray emission does not make use of any spin detector or circular-polarized X-rays, but instead uses an internal spin reference, namely, the intermediate state with its 1s core hole. It has been eluded already in section III that 1s2p and 1s3p X-ray emission spectra are spin-polarized. In all models discussed to interpret these spectra there will always be a small exchange interaction between the 1s core hole and the 3d electrons. The result is that in the calculations each transition is essentially split into two subpeaks split by the 1s3d exchange. The energies involved are only a few meVs, and as a result there will be no visible effects in the spectral shape. So why is this an interesting and in fact very useful effect?

The reason is that in the final state the configurations are 3p3d and, as discussed, the 3p3d exchange interaction is very large, creating in a first approximation a main peak that is spin-up and a satellite at some 15 eV distance that is spin-down. Things are not as easy as this simple division, and to calculate the actual division into spin-up and spin-down, it is very useful to make use of the small 1s3d exchange interaction in the calculations. Because the 1s2p and 1s3p X-ray emission channels will conserve their spin state, the two 1s intermediate states will essentially map the spin-up and spin-down states, refer to the paper of Wang and co-workers for details.121
Figure 32 shows the separation into spin-up and spin-down using ligand-field multiplet calculations. The situation does not change significantly if one includes charge transfer. One can immediately see that the 1s2p X-ray emission spectra only have a minor separation into spin-up and spin-down. Both the main peak and the satellite essentially show a shift between spin-up and spin-down. The situation is completely different in the case of the 1s3p X-ray emission spectra. Here a pure spin-down peak is seen for the satellite, while the main peak is mostly spin-up. This is particularly clear in the middle of the series where the exchange interaction is largest. It is because of this difference between 1s2p and 1s3p spectra that the 1s3p spectra can ideally be used to perform spin-selective X-ray absorption experiments that will be discussed in section VII.

VII. Selective X-ray Absorption

Selective X-ray absorption is an experiment that makes use of a particularly chosen X-ray emission decay channel. One could also use a photoemission/Auger channel, but these experiments will not be discussed in this paper. The onset of selective X-ray absorption can be found in the work of Hämäläinen and co-workers, who showed that selective X-ray absorption effectively removes the lifetime broadening and who later showed the possibility of measuring spin-dependent X-ray absorption.

In section V, it was pictorially shown that the lifetime broadening effectively is removed if one measures selective X-ray absorption at resonance. Here the discussion on lifetime broadening disappearance will be extended. Figure 33 shows schematically the excitation of a 1s core electron at 3000 eV to the edge. One detects the 3p electrons that decay to the 1s hole. The detector is set at an energy equal to the binding energy of the 3p state. In that case, it does not matter if the top or bottom transitions do take place (see text).

The summation of the X-ray emission matrix element yields a constant \( \langle \Phi | \hat{r} | \Phi \rangle^2 \) and can be removed from the formula. What remains is analogous to the normal XAFS:

\[
I(\omega) \sim \sum_x \sum_i (\langle \Phi_i | \hat{r} | \Phi_x \rangle^2 (\langle \Phi_i | \hat{r} | \Phi_x \rangle^2 (21)
\]

The sumation of the X-ray emission matrix element yields a constant \( I_{XES} \) and can be removed from the formula. What remains is analogous to the normal XAFS.
Functional form for selectivity is given by
\[ I(\omega) \sim \sum_x (\Phi_x|\hat{\mathbf{r}}|\Phi_i)^2 \delta_{E_F-E_i-(\hbar\omega-h\omega_0)}. \]  

It can be seen that the matrix element concerns the intermediate-state \( \Phi_x \), for example, a 1s state, and the delta function (that is rewritten to a Lorentzian broadening) contains the final state and initial state, without the intermediate state. In other words, the lifetime broadening of the intermediate state is completely removed from the equation. In section V it was shown that in the case of 2p core holes, interference effects modify this picture a little bit, but the essential conclusion remains that selective X-ray absorption can measure X-ray absorption spectra with a resolution much better than the core hole lifetime broadening.

It was shown that the combination of X-ray absorption and X-ray emission gives us (a) lifetime broadening removed X-ray absorption and (b) spin-, valence-, and site-selective X-ray absorption.

A. Lifetime Broadening Removed X-ray Absorption

One can make use of one of these possibilities to improve upon the normal 2p X-ray absorption experiments. That is, one can remove the 2p lifetime broadening of ca. 4 eV and replace it by the 3d or 4d lifetime broadening of less than 0.5 eV. This results in enormously sharper L\(_{2,3}\) edges. Figure 34 shows the platinum L\(_3\) edge measured with fluorescence yield XAFS (\(\cdots\)) and with 2p\(_{3d}\) detected XAFS (\(\cdots\)).

![Figure 34](image)

Figure 34. Platinum L\(_3\) edge measured with fluorescence yield XAFS (\(\cdots\)) and with 2p\(_{3d}\) detected XAFS (\(\cdots\)).

the platinum L\(_3\) edge with fluorescence yield X-ray absorption (points) and with 2p\(_{3d}\) detected X-ray absorption (dashed), both measured simultaneously at beamline ID26 at ESRF. Details on the experiment and the analysis will be published elsewhere. As expected, the L\(_3\) is sharper if the 2p lifetime broadening is removed. This sharpening makes it possible to measure the L\(_3\) edge with very high resolution, provided the monochromator resolution is very good. The high-resolution XANES spectra can be used to study small variations in the lowest empty states.

B. Valence-, Spin-, and Site-Selective X-ray Absorption

The central point of selective X-ray absorption is to make use of a particular fluorescence channel to measure the X-ray absorption spectrum. For example, by measuring the X-ray absorption spectral shape at the peak positions of the K\(_{\beta1,3}\) and the K\(_{\beta'}\) peaks, one can obtain the spin-selective X-ray absorption spectral shape.\(^{33,121}\) This is important for the study of magnetic materials. This applies not only to the XANES region, but just as well to the EXAFS region, which allows for studies on the local geometry that are, for example, separated for their spin.\(^{119,120}\)

1. Valence-Selective X-ray Absorption

As shown in Figure 15, the 1s3p fluorescence spectral shapes shift to higher energy with increasing valence. One can tune the energy of the fluorescence detector to the peak position of one valence and vary the energy of the incoming X-ray, thereby measuring the X-ray absorption spectrum of that particular valence. This can be repeated for the other valence. Consequently, one obtains separate X-ray absorption spectra for the various valences present, in other words valence-selective X-ray absorption.\(^{115}\)

Recently, valence-selective X-ray absorption has been applied to Fe\(^{II}\)(Fe\(^{II}\)(CN)\(_6\))\(_3\) (Prussian Blue). Prussian Blue can be considered the prototype of mixed-valence compounds. It contains two kinds of iron in different oxidation and spin states. The ferrous ion presents a coordination shell constituted by six carbons at 1.92 Å and is surrounded by six nitrogens at 3.04 Å and six ferric ions at 5.08 Å. The formal oxidation number is II, and the strong crystal field exhibited by the carbon atoms yields a low-spin ground-state configuration. The ferrion Fe\(^{II}\) has a high-spin configuration. The bulk ratio Fe\(^{II}\) to Fe\(^{II}\) is 4:3. Glatzel and co-workers\(^{154}\) showed that the 1s3p X-ray emission spectrum of Prussian Blue can be simulated by a 4:3 ratio of the spectra of Fe\(_2\)O\(_3\) and K\(_4\)Fe(CN)\(_6\). Using these two systems as a reference for the Fe\(^{II}\) and Fe\(^{II}\) spectra, valence-selective X-ray absorption spectra were measured by tuning the crystal analyzer to fluorescence energies that mainly detect contributions from the element in one specific site while the energy of the incident X-ray beam is scanned through the iron K-edge region, including the EXAFS. EXAFS analysis shows good agreement of the Fe\(^{II}\) and Fe\(^{II}\) sites with X-ray diffraction data.\(^{154}\)

2. Spin-Selective X-ray Absorption

Figure 32 in section V.E explained the measurement of spin-polarized X-ray emission spectra. Tuning the detector to a photon energy related to either spin-up or spin-down while scanning through an absorption edge, the spin-polarized X-ray absorption spectrum is measured. From Figure 32b, it is evident that Mn\(^{II}\) is the ideal case to carry out spin-selective X-ray absorption. It turns out that the critical parameter is the number of unpaired 3d electrons. The strong 3p3d exchange interaction will create large splittings that reach a maximum for high-spin 3d\(^5\). The spin-selective X-ray absorption spectrum can be measured for all systems that carry a local moment on a transition-metal ion. This includes ferromagnets, antiferromagnets, and paramagnetic systems.

Spin-selective X-ray absorption was measured for the first time by Hämäläinen and co-workers.\(^{156}\) By
detecting the main peak and the satellite of the 1s3p X-ray emission spectrum of the antiferromagnet MnF₂, they could measure separate X-ray absorption spectra for spin-up and spin-down. It is interesting to compare the spin-selective X-ray absorption spectrum with the MCD spectrum of ferromagnets. For ferromagnets, the spin-selective X-ray absorption spectrum identifies with the spin-polarized density of states. As discussed in section IV.A (eq 20), K-edge MCD measures the spin-polarized density of states times the Fano factor. By measuring both the MCD and the spin-selective X-ray absorption spectra of the same system, one is able to determine directly the magnitude of the Fano factor, including its potential energy dependence. Measurements on a ferromagnetic MnP sample did show a large energy dependence of the Fano factor, reaching ~4% at the edge and decreasing to a much smaller value above the edge.43,44

The measurement of spin-selective X-ray absorption is easiest for 3d⁸ systems. This, however, does not imply that spin-selective X-ray absorption is impossible for systems that have only one or two unpaired electrons. Recently, Wang and co-workers measured the spin-selective X-ray absorption spectrum of the high-spin NiII system (PPh₄)₂Ni(SePh)₄. Using the spin-polarized signal of the 1s2p X-ray absorption opens a large range of new series of experiments, but the intrinsic low intensity will make it very hard experiments too.

A final possibility is site-selective X-ray absorption. This possibility arises from the oxygen to metal crossover decay channel, i.e., the K/β peak in Figure 16. Because the oxygen 2s peak is present only for the metal atoms that are neighbors to the oxygen, one can measure the X-ray absorption spectra of only those metal atoms. It is important to note that the X-ray absorption (including EXAFS) analysis is essentially the same as for normal X-ray absorption and all atoms surrounding the excited atom do contribute to the electron scattering. Only the X-ray excitation and decay process is specific for one type of neighbor, while the electron scattering determining the X-ray absorption spectral shape is not. Site-selective X-ray absorption opens a large range of new series of experiments, but the intrinsic low intensity will make it very hard experiments too.

It can be concluded that selective X-ray absorption provides a new useful tool for the study of systems that contain an element in two distinct situations. This adds an extra advantage to the element selectivity of normal X-ray absorption. Because only hard X-rays are involved, further applications are envisaged in situ characterization in fields such as electrochemistry, heterogeneous catalysis, high-pressure studies, etc.

VIII. Conclusions and Outlook

In this paper a review of high-resolution X-ray emission and X-ray absorption experiments has been given. The emphasis has been on the fundamental aspects of the interpretation and, in addition, on recent advances in this field. The enormous amount of (high-resolution) X-ray emission literature from nonsynchrotron sources has been largely neglected.

In conclusion, it can be remarked that at present there is a situation in which X-ray absorption spectra are analyzed either with density functional theory for the 1s core levels or multiplet theory for all other edges. X-ray emission always involves a core level that necessitates multiplet analysis of the spectral shape. The field of high-resolution X-ray emission is still in a stage of large experimental progress, and more and higher resolution spectra are expected soon. This will in turn cause the theoretical interpretations to become more refined. Some examples of this development are the detection of spin-flip transitions and the realization that Coster–Kronig channels are important for a good description. A picture of X-ray emission will never be complete without the equivalent understanding of the nonradiative decay channels, i.e., resonant photoemission and Auger.

Because high-resolution X-ray emission is a relatively new technique at synchrotron radiation sources, a large part of the experiments carried out today and in the past can be envisioned as prototype experiments. As such, they often belong to the realm of physics. However, a number of dedicated hard X-ray emission beamlines are projected and/or build at least at the APS, ESRF, and HASYLAB. New soft X-ray emission (resonant inelastic X-ray scattering) beamlines are present at, for example, ALS, MAXLAB, and ELETTRA. These beamlines will make techniques such as RIXS and selective X-ray absorption more accessible to nonexperts, and it is expected that this will largely extend the scope of experiments to be performed. It is hoped that this review serves as a good starting point for the planning of these experiments in fields such as (bio)catalysis, coordination chemistry, electrochemistry, magnetic devices, surfacscience, etc.

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X. References
