

2p x-ray absorption of 3d transition metal compounds

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ABSTRACT

In this paper we describe the analysis of 2p x-ray absorption of 3d transition-metal compounds. For the analysis an atomic multiplet approach with inclusion of the crystal field is used. This approach has potential use for the determination of the surroundings and of the local electronic and magnetic structure of the 3d transition-metal in any material. A justification for the use of the model is given.

Introduction

Due to the improved resolution in the soft x-ray range [1], 2p x-ray absorption of the 3d transition metal compounds shows a large amount of new fine structure at the edge. Analysis made clear immediately that any detailed description needs the inclusion of the core hole effects, for all the multipole 2p-3d Coulomb and exchange interactions. Therefore a general computational scheme, based on atomic multiplet theory and group theory, has been developed. To outline the position of the multiplet theory in the range of models for x-ray absorption near edge structure, we present a short overview of some of the 1-particle as well as many-body approaches.

Single particle approaches

The interaction of x-rays with matter is generally described by the dipole matrix element squared times a delta function (conservation of energy): the Fermi Golden Rule [2]. In the single particle approach the many-electron wavefunction is approximated by a single Slater integral.

The most common approach is to use effective 1-particle functions for the core electron and the (empty) final state. This transforms the Golden Rule to a matrix element

squared times the (dipole) projected Density of States (DOS) A further approximation is to neglect the core hole (and correlation) completely, in which case one can simply use the 'ground state' DOS calculation, using either Density Functional Theory (DFT) [3] or Multiple Scattering [4]. The core hole can be included as a potential in the final state DFT (and MS) calculations, which are under development [5]. These final state calculations are however (computer)time consuming, which makes it attractive to simulate the final state DOS, using the 'ground state' result and the Clogston-Wolff model[6].

Instead of these 1-particle DOS approaches one can also use a multiplet approach, in which the x-ray absorption process in a first approximation is described atomically. This offers the possibility to include the multipole core hole effects and the multipole effects in the 3d-band; The atomic 2-electron integrals $\langle 2p3d | H | 2p3d \rangle$, $\langle 2p3d | H | 3d2p \rangle$ and $\langle 3d3d | H | 3d3d \rangle$. Using a Hartree-Fock approximation, thus within the 1-particle limit, the calculation gives a number of discrete lines related to all possible dipole-transitions from the $3d^N$ initial state to the $2p^5 3d^{N+1}$ final states. In our calculations a cubic crystal field term is added to the Hamiltonian, to include solid state effects. The cubic crystal-field coupling is treated as a free parameter to be varied to obtain the best fit to experiment.

The choice of whether the multiplet model or DFT/MS is more appropriate, is related to the importance of the hybridization effect versus the correlation effects, and to the importance of multipole effects of the core hole. Thus for the 3d transition metal compounds the metal 1s edge as well as the ligand 1s edge are best approximated with DFT/MS, whereas for the metal 2p edge the multiplet scheme is preferred.

Many-Body effects

Many body effects can give rise to extra satellite structure and are, for the description of x-ray absorption, generally accounted for by model-Hamiltonians. A typical model is that of Mahan-Nozieres-DeDominicis (MND), which accounts for the edge anomalies in simple metals due to the change in the valence band 2-electron integrals. For absorption to a strongly correlated state, the Anderson Impurity Hamiltonian, which takes into account charge transfer to the ligand (L), thus the mixing of $d^N + d^{N+1}\underline{L}$, is more appropriate [7]. As in x-ray absorption, in contrast to x-ray photo-emission, the charge is conserved locally, the amount of mixing is in general not changed much, which results in small, or non-existent, satellites. Instead of the mixing in of charge transfer excited states also polaronic excited states can be mixed in the ground state. Polaronic excitations can be described as $d^N + d^N\underline{LL}'$; the polarization of the ligand [8]. If this mixing is changed due to the core hole, it gives rise to satellites[9].

Multiplet calculations

The effectiveness of the multiplet approach in describing the 3d transition-metal compounds has been shown for empty d-bands[10] respectively partly filled d-bands[11]. In figure 1 we show as examples the 2p XAS spectra of ScF_3 and MnF_2 . Due to the excellent agreement with experiment, it is possible to determine the valency and the spin-state. Also the cubic crystal-field parameter (10Dq) can be determined quite accurately. This analysis can be improved upon, if angular dependent spectra are measured (on ordered materials) using linear or circular polarized soft x-rays. The polarization dependent spectra reveal the ground state more accurately. Information can be gained on all other crystal-field parameters and the magnetic moment, by adding terms to the Hamiltonian and varying the parameters to find the best fit to experiment.

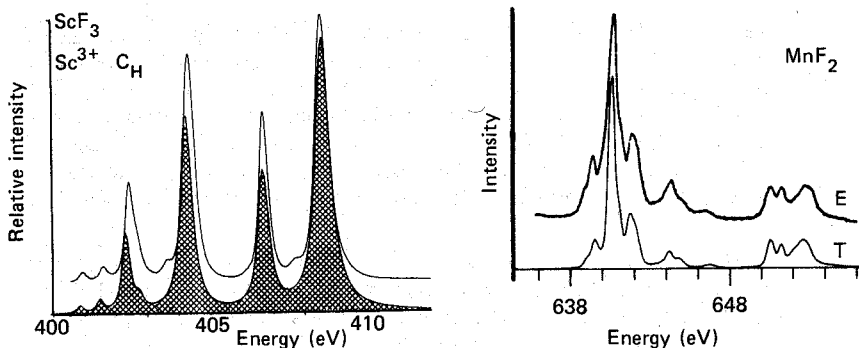


Figure 1. Comparison of the 2p XAS edge of ScF₃ and MnF₂ with a multiplet calculation of resp. d^0 Sc³⁺ (10Dq=1.8 eV) and of d^5 Mn²⁺ (10Dq=0.9 eV). The experiments were performed by F. Sette and C.T. Chen using the DRAGON monochromator at NLSLS, Brookhaven. (The TOP spectra are experimental (E)).

This richness of results from the detailed multiplet analysis, can be combined with the other features of x-ray absorption. Because XAS is a local process it is element specific. This can be used to study the local structure of 3d transition metals. Using the different probing depths of the possible detection techniques one can change XAS from a bulk-technique to a surface technique, using resp. fluorescence yield, total electron yield, partial electron yield and ion-yield. One can use this to study the possible surface effects on the crystal field parameters and the magnetic moment.

Conclusion

It can be concluded that 2p x-ray absorption of 3d transition metal compounds, analyzed with the multiplet model, offers a potentially powerful method for the analysis of the local crystal, electronic as well as magnetic structure of 3d transition metals. This can be used in fields as bio-inorganics, mineralogy and magnetic media.

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