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Differences between L_3 and L_2 X-ray absorption spectra

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Abstract

The L_3 and L_2 edges of transition metals show differences in their spectral shape. Also the ratio between the L_3 and L_2 edges is found to deviate from 2:1. The interactions responsible for these effects are: the multiplet effects and the 3d (4d) spin–orbit coupling. The electronic interactions and spin- and orbital polarizations of the valence electrons determine the ground state (symmetry) and determine the shape itself. For 4d systems the L_3 and L_2 are separated by a large core spin–orbit splitting of about 100 eV. Differences between their L_3 and L_2 edge originate from the weight transfer between the t_{2g} and e_g peaks due to the multiplet effects. Because this weight transfer is larger for L_3 edge, it is better to use the L_2 edge for a comparison to single particle calculations. The only interaction which can affect their branching ratio is the 4d spin–orbit coupling. For 3d systems the multiplet effects dominate all other interactions and the L_3 and L_2 are completely different and show their characteristic multiplet structure. The multiplet effects are large enough to affect also the branching ratio.

1. Introduction

The differences between the L_3 and L_2 edges are analysed theoretically. Within non-relativistic single particle models the L_3 and L_2 edges should be equivalent. The intensity of the L_3 edge ($j_{\mathrm{core}} = 3/2$) is two times that of the L_2 edge ($j_{\mathrm{core}} = 1/2$) and they are separated by 3/2 times the core spin–orbit coupling (ξ_{2p}). Experimentally it is found that the L_3 and L_2 edges often show differences [1, 2] and it is known that also their ratio differs from 2:1. This (branching) ratio has been thoroughly studied by Thole and van der Laan [3, 4], who concluded that the ratio can only be affected by two effects: (a) the initial state d spin–orbit coupling (ξ_d) and (b) the overlap between the 2p wave function and the d wave function, the so-called multiplet effects. The multiplet effects are given with the Slater integrals F^2, G^1 and G^3 [5].

The origin for the differences in shape between the L_3 and L_2 are similar. Again the d spin–orbit coupling (ξ_d) and the multiplet effects are important. Also important for the shape are the electronic structure properties and the spin and orbital polarizations of the d electrons. To show the relative importance of these interactions the crystal field multiplet model is used [6]. This model has been shown to simulate closely the L_3 and L_2 edges of both 3d [7] and 4d [2] transition metal compounds.

2. Systems with an empty d band

For an empty d band the transition is from d^0 to $2p^5d^1$. With a single particle model the L_3 and L_2 edges are described by the transitions to the empty d states which can be determined from electronic structure calculations. They have an intensity ratio of 2:1 and are separated by $3/2\,\xi_{2p}$. To simplify the multiplet calculations the electronic structure is approximated with just a cubic crystal field (Δ_C). Then the spectral shape shows two peaks for both the L_3 and L_2 edge with an intensity ratio of 6:4 and separated by Δ_C.

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Because the d band is empty there are no initial state effects. Potential effects come from final state d spin-orbit coupling and multiplet effects. It turns out that the final state effect from ξ_d is small and modifies the intensities only a few percent [2]. The multiplet effects are much larger. The Slater integrals and characteristic crystal field strength are given in Table 1. The size of the effect depends on the comparison of the multiplet effects (F^2; G^1; G^3) and the energy difference of the states (given by Δ_C). Their ratio shows that for the 2p edge of 3d systems the multiplet effects are bigger than for the corresponding 4d systems, though for 4d systems the effect is still sizeable. Fig. 1 compares the experimental spectrum of MoF_6 with a crystal field multiplet calculation. A cubic crystal field of 4.5 eV was fitted to the experiment. The theoretical line spectrum was broadened with a lifetime broadening ($2\Gamma = 2.0$ eV). The spectrum was then convoluted with a Gaussian ($\sigma = 0.4$ eV) to simulate the experimental broadening. The L_3 and L_2 spectra have been aligned with respect to the calculated ones. The L_3 and L_2 edges, including their difference, are reproduced. Analysing the spectral shapes in detail it turns out that the L_3 edge is much more affected by the multiplet effects than the L_2 edge. From this one can conclude that if one compares to single particle density of states, it is preferable to use the L_2 spectral shapes [2].

Table 1
Excitation energy, Slater integral (F^2_{pd}), 2p spin-orbit coupling (ξ_{2p}) and characteristic crystal field strengths (Δ_C) for the 2p edges of Fe^{3+} and Ru^{3+}. All values are given in eV

Ion	Energy	F^2_{pd}	ξ_{2p}	F^2_{pd}/ξ_{2p}	Δ_C	F^2_{pd}/Δ_C
Fe^{3+} ($3d^5$)	700	7.5	13	0.57	1.0	7.5
Ru^{3+} ($4d^5$)	2900	2.1	130	0.02	3.0	0.4

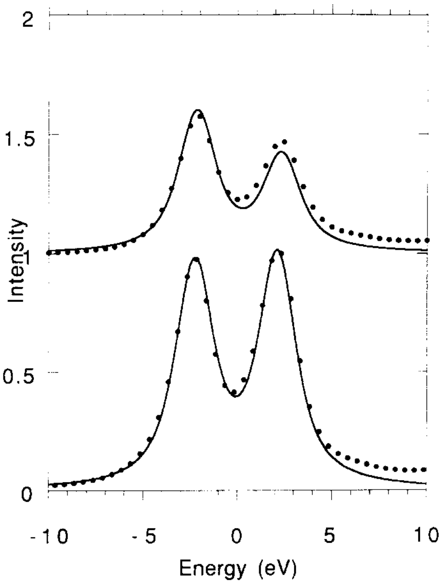

Fig. 1. Comparison of a crystal field multiplet calculation of Mo^{6+}, $4d^0$ (solid line) with an experimental spectrum of gas-phase MoF_6 (points). The L_2 edge (top) and the L_3 edge (bottom) have been aligned. A crystal field strength of 4.5 eV was used.

The 3d systems are affected strongly and their L_3 and L_2 edges are considerably different. Because the multiplet effects are so large one splits off peaks which relate to 'forbidden transitions' in a single particle model [5]. For 3d systems the multiplet effects are large enough to influence also the branching ratio. Experimentally it is found that while 4d systems with an empty d-band obey the 2:1 rule, 3d systems show strong deviations in close correspondance to the predictions from multiplet theory. In fact most $3d^0$ compounds show an L_2 edge which is more intense than the L_3 edge [5].

3. Systems with a partly filled d band

Systems with a partly filled d band are subject to strong intra-band dd correlation effects, described with F^2 and F^4 Slater integrals. In solid state theory these dd Slater integrals are rewritten to the exchange splitting and the orbital polarization [8]. Together with the crystal field they determine the symmetry of the ground state by maximising (1) the spin and (2) the orbital moment (Hund's rules). The action of the d spin-orbit coupling on the ground state is important, both for the spectral shape and the branching ratio. Fig. 2 shows the results of crystal field multiplet calculations for the L_3 (solid) and L_2 (dashed) spectra of molybdenum for the configurations $4d^0$ (bottom) to $4d^6$ (top). The spectra have been aligned and normalised to the peak height of the L_3 edge. The L_2 edge is multiplied by two. A crystal field splitting of 4.0 eV has been used and as a result all $4d^n$ states are in a low-spin ground state. Both the 4d spin-orbit coupling and the multiplet effects make that the L_3 edges are different from the L_2 edges. Going from the bottom to the top, both for the L_3 and the L_2 edge the intensity of the first peak decreases. The reason is that the t_{2g} band contains more and more electrons and is completely filled in the top $3d^6$ spectrum. The decrease of the t_{2g} peak is stronger for the L_2 edge and for a $4d^5$ ground state the t_{2g} peak even disappears for the L_2 edge. The reason is that due to the 4d spin-orbit coupling some transitions are forbidden for the L_2 edge [2].

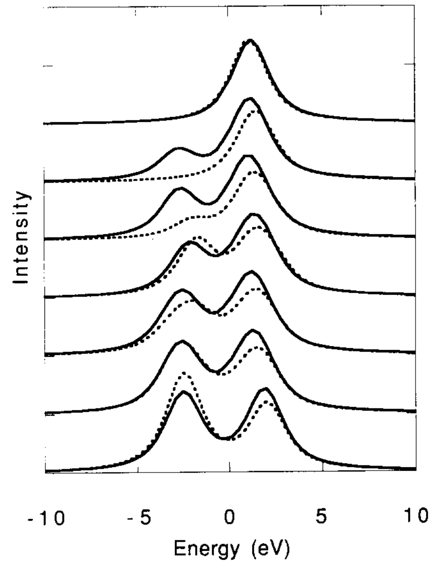

Fig. 2. Crystal field multiplet calculations for molybdenum. The L_3 edge (solid line) and the L_2 edge (dashed) are given for $4d^0$ (bottom), $4d^1$, $4d^2$, $4d^3$, $4d^4$, $4d^5$ and $4d^6$ (top) ground state configurations. Crystal field strengths of 4.0 eV were used.

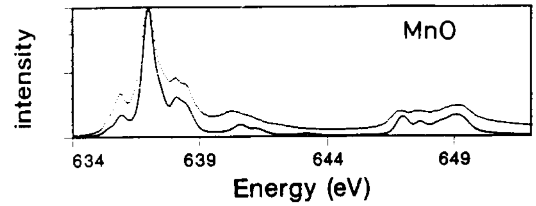

Fig. 3. Manganese 2p X-ray absorption spectrum of MnO (dotted) compared with a crystal field multiplet calculation (solid line). A crystal field strength of 0.8 eV was used.

For 3d systems the spectral shape is completely dominated by multiplet effects and any similarity to the single particle density of states has disappeared. As an example Fig. 3 shows the 2p X-ray absorption spectrum of MnO compared with a crystal field multiplet calculation [1]. The L_3 and L_2 edge are completely different and show a many-peaked spectrum related to the $2p^5 3d^6$ excitonic-like states. The importance of the 3d spin–orbit coupling can be nicely shown for CoO. CoO has a $3d^7$ ground state of $^4T_1$ symmetry. The 3d spin–orbit coupling splits this ground state into four separate states, each with a clearly different spectral shape given in Fig. 4. The comparison with experiment (given in Ref. [9]) reveals that the actual ground state is dominated by the E_2 state. With a temperature dependent study one is able to determine the precise value of the 3d spin–orbit coupling.

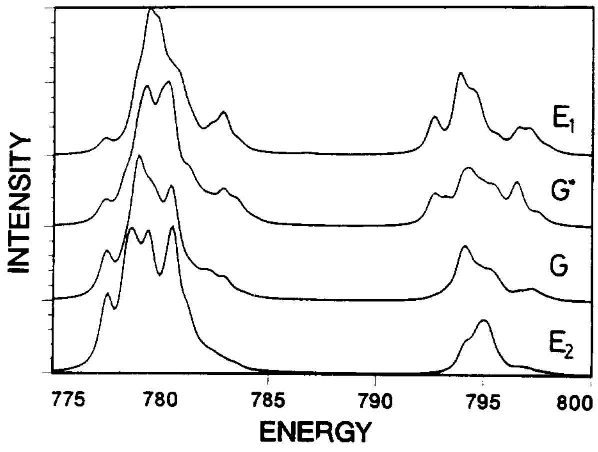

Fig. 4. Crystal field multiplet calculations for the transition from a high-spin $3d^7$ state as present in CoO. The spectra of the four spin–orbit split configurations are shown. A crystal field strength of 0.8 eV was used.

The experimental branching ratio changes strongly over the 3d series as demonstrated for the pure 3d metals by Fink and coworkers [10]. This trend is reproduced directly from multiplet calculations [6]. The main reason for the strong variations in the branching ratio is that the early transition metals have relatively small ξ_{2p} which makes the influence from the multiplet effects large.

4. Concluding remarks

The *shape* of L_3 and L_2 edges is determined by the crystal field strength, the spin and orbital polarizations and the d spin–orbit coupling (present in initial plus final state) as well as by multiplet effects (only present in the final state).

The *difference in shape* of L_3 and L_2 edges is caused by the relative importance of the multiplet effects. 3d systems are completely dominated by multiplet effects. The d spin–orbit coupling also causes differences in shape by affecting the ground state symmetry.

The *difference in intensity ratio from* 2:1 is caused by the initial state d spin–orbit coupling. For the early 3d metals also the multiplet effects significantly affect the intensity ratio.

Acknowledgements

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