Multiplet effects in the Ru-L2,3 x-ray absorption spectra of Ru(IV) and Ru(V) compounds


DOI
10.1103/PhysRevB.61.5262

Publication date
2000

Published in
Physical Review B

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (https://dare.uva.nl)
Multiplet effects in the Ru $L_{2,3}$ x-ray-absorption spectra of Ru(IV) and Ru(V) compounds

Z. Hu, H. von Lips, M. S. Golden, and J. Fink
Institute for Solid State Research, IFW Dresden, D-01171 Dresden, Germany

G. Kaindl
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany

F. M. F. de Groot
Department of Inorganic Chemistry, University of Utrecht, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

S. Ebbinghaus and A. Reller
Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

(Received 5 August 1999)

We report combined experimental and theoretical investigations of x-ray absorption at the Ru-$L_{2,3}$ and O-K thresholds of the Ru(IV) compounds RuO$_2$ and Sr$_2$RuO$_4$ and of the Ru(V) compound Sr$_3$Ru$_2$O$_7$. Significant differences in the intensity distribution of the $t_{2g}$-related and $e_g$-related peaks between the $L_3$ and the $L_2$ edges are found, due to the combined effects of $4d$ spin-orbit coupling and the interelectronic Coulomb interaction described by the Slater integrals. The observed spectral features can be well reproduced by crystal-field-multiplet calculations. With increasing the Ru valence from IV to V, the spectra are shifted by $\approx 1.5$ eV to higher energy at the Ru-$L_{2,3}$ edges and $\approx 1.0$ eV to lower energy at the O-K edge, which is of the same order of magnitude as on going from the divalent to the trivalent late 3$d$ transition-metal oxides.

I. INTRODUCTION

Correlation effects are well known in the x-ray absorption spectra (XAS) of the 3$d$ transition-metal (TM) $L_2$ and $L_3$ edges, and can be well reproduced using crystal-field-multiplet calculations (CFMC) by combining atomic multiplet programs with group theory in a crystal field. In contrast, it has often been assumed that the $L_{2,3}$ spectra of the 4$d$ TM compounds reflect directly unoccupied 4$d$ orbitals influenced by the local symmetry of the metal ion, and spectra have been interpreted in terms of crystal-field or molecular-orbital theories. In this context, the single peak observed at the Ru-$L_2$ edge and the two peaks at the Ru-$L_3$ edge of Ru(NH$_3$)$_6$Cl$_3$ (which has a Ru 4$d^5$ configuration and octahedral symmetry) were explained in terms of vanishing matrix elements for the transitions at the $L_2$ edge into the $t_{2g}$ orbitals resulting from consideration of the 4$d$ spin-orbit coupling within a single-particle treatment. On the other hand, detailed CFMC resulted in multiplet spectra with a single peak at the $L_2$ and a double peak at the $L_3$ edge for a 4$d^5$ configuration. Thus, both the 4$d$ spin-orbit and the CFMC approaches can account for the XAS data of 4$d^5$ systems.

The differences between the two theoretical approaches become interesting in the case of a 4$d^4$ system. In this case, the 4$d$ spin-orbit argumentation used in Ref. 7 predicts that a 4$d^4$ compound should have the same single peak at the $L_2$ edge as is the case for 4$d^5$. In contrast, CFMC calculations predict a double-peaked structure at both the $L_2$ and $L_3$ edges. Thus it is unclear to what extent the single-particle treatment or the CFMC approach represents the correct theoretical background in which to rationalize the experimental $L_{2,3}$ XAS spectra in 4$d$ electron systems.

II. EXPERIMENT

The Ru-$L_{2,3}$ XAS spectra of polycrystalline RuO$_2$, Sr$_2$RuO$_4$ and Sr$_3$Ru$_2$O$_7$ were recorded in transmission geom-
MULTIPLET EFFECTS IN Ru L2,3 X-RAY-... 

The Ru ions in the three compounds studied have basically an octahedral coordination and therefore experience a crystal field with O₆ symmetry resulting in the splitting of the 4d states into t₂g (dₓ²−y², dₓz, dᵧz) and e₉ (dₓ²−y², dₓz, dᵧz) levels separated by Δ = 10 Dq. In general, within the single-particle model two peaks are expected at both the L₂ and L₃ edges corresponding to 2p→t₂g and 2p→e₉ transitions for the configuration d⁶ to d⁵ (we neglect here the weak 2p→n5 transition, n≥5). For the configurations d⁶ to d⁹, the 2p→t₂g channel is closed, and a single peak related to 2p→e₉ transitions is expected. However, upon consideration of the 4d spin-orbit coupling, the transitions to some of the crystal-field-split orbitals become forbidden. Figure 1 shows schematically an energy-level diagram of the 4d orbitals as they successively experience (i) an octahedral field, (ii) a spin-orbit splitting, and (iii) a weak tetragonal distortion. Forbidden transitions marked with ‘‘XX’’ are obtained by calculations of the transition matrix elements using the crystal-field-orbital wave functions, Γ₁₂,Γ₃₄,Γ₁₂,Γ₃₄, listed here in order of increasing energy. From Fig. 1, one can predict that, within this single-particle spin-orbit scenario, at the L₂ edge the 2p→t₂g channel is closed for 4d occupation equal to or exceeding four electrons, and only one peak is expected in the L₂ x-ray absorption spectrum. As was mentioned earlier, this is experimentally found to be the case for the 4d⁹ configuration present in the Ru(III) systems Ru(NH₃)₆Cl₃ and K₃RuCl₆.⁴,⁷ We now turn our attention to the experimental situation for 4d⁴ systems. The L₂ absorption edges of the Ru(IV) systems RuO₂ and Sr₂RuO₄ as well as the Ru(V) system Sr₂Ru₂O₅ are shown in Fig. 2 (the latter will be dealt with later). To ease comparison, the L₂ spectra (open symbols) have been shifted in each case such that the high energy feature (B) is aligned with the corresponding feature in the L₃ spectra (filled symbols). The L₂ spectra have also been multiplied, in the case of both 4d⁴ systems, by a factor of 2.15. The spectra of the Ru 4d⁴ systems exhibit two peaks (denoted as A and B), at both the L₃ and L₂ edges. The lower energy peak A and the higher energy peak B can be basically assigned to 2p→t₂g and...
2p→\epsilon_g transitions, respectively. The observed spectral features thus clearly indicate that the 2p→t_{2g} excitation channel is not closed at the Ru-L_2 edge for the 4d^4 configuration, indicating that the single-particle approach illustrated in Fig. 1 is certainly not the whole story. What is missing in this approach is an adequate treatment of the 2p/4d correlation effects. For 3d TM compounds these effects are comparable with the spin-orbit coupling of the 2p core hole, resulting in a strong transfer of intensity between the L_2 and L_3 edges, and are also stronger than the crystal-field splitting, resulting in a more complex multiplet structure. For the 4d TM elements, the 2p/4d coupling amounts to ≈2–3 eV, and is thus much smaller than the spin-orbit splitting of the 2p level (larger than 100 eV), and consequently the correlation effects have no influence on the L_1 and L_2 intensity ratio. However, the 2p/4d coupling is of the same magnitude as the crystal-field strength (10Dq) and can therefore result in a transfer of intensity between t_{2g}-related and \epsilon_g-related final states. It should also be noted that although the 4d/4d multiplet interaction and the 4d spin-orbit coupling are one order of magnitude smaller than the crystal-field strength, they determine the symmetry of the wave functions of the 4d state, thus in turn determining the intensity of the transitions. Thus, bearing in mind that the L_2 data for the Ru(IV) systems shown in Fig. 2 are already multiplied by 2.15 in order to match the intensity of the L_1 spectra at feature B, the combined effects of correlation and the 4d spin-orbit coupling lead to the observed suppression of the t_{2g}-related L_2 spectral weight for both RuO_2 and Sr_2RuO_4 in comparison with the analogous feature in their L_3 edges.

We now turn to the Ru(V) compound Sr_2Ru_2O_9, which has a 3d^5 configuration. From Fig. 1 (single-particle model) we would expect that the t_{2g}:\epsilon_g ratio is smaller at the L_2 than at the L_3 edge, because of the forbidden nature of the transition to the \Gamma_2,2 orbital. However, the relative intensity of the t_{2g}-related peak A for Sr_2Ru_2O_9 in Fig. 2 is greater at the L_2 edge than at the L_3 edge. Once again we see that the predictions of the single-particle picture are not sufficient to explain the observed 4d^1 L_3 XAS spectrum. Comparing now the Ru(V) with the Ru(IV) systems, we note that on increasing the Ru valence, the double-peaked L_2 and L_3 edges are shifted by 1.5 eV to the higher energy. This shift is very similar to those observed in the Ni or Cu-L_{2,3} XAS spectra on going from Ni(II) to Ni(III) or from Cu(II) to Cu(III) in 3d TM systems.\(^{17}\)

In order to understand the observed XAS spectra in detail we have performed a series calculations within the CFMC approach, which are presented in the next section.

**IV. CALCULATIONS**

The Hamiltonian for the crystal-field-multiplet calculations is written as

\[ H = H_{av} + H_{MS}. \]  

(1)

\( H_{av} \) gives the average energy and does not contribute to spectral splittings, while \( H_{MS} \) includes all contribution to splittings given by

\[ H_{MS} = \mathbf{L} \cdot \mathbf{S}(2p) + H_{\text{CFMC}} + \mathbf{L} \cdot \mathbf{S}(4d) + g(ij). \]  

(2)

For 4d TM compounds the large spin-orbit splitting of the 2p core hole merely separates the L_3 and L_2 edges into two groups of spectra, and does not contribute to the splittings for each edge. The spectral structures are determined by the cubic crystal field, \( H_{\text{CFMC}} \), the two-electron Coulomb term, \( g(i,j) \), as well as the spin-orbit splitting of the 4d electron, \( \mathbf{L} \cdot \mathbf{S}(4d) \). The \( g(i,j) \) term is required to account for “multiplet effects” and its importance will be emphasized in the following. The radial part of \( g(i,j) \) is divided into a direct Coulomb term \( F^a \) and an exchange term \( G^a \) — the so-called Slater integrals. In this work the degree of reduction of the Slater integrals from their atomic values is taken as a free parameter to simulate the effects of hybridization in solids, known as nephelauxetic effects.\(^{18}\)

The right panel of Fig. 3 shows the calculated Ru-L_3 (solid line) and Ru-L_2 (dashed line) XAS spectra for a 4d^4 Ru(IV) configuration using 10Dq = 2.5 eV and multiplied by 2.9. The atomic value of the Slater integrals are \( F^2(pd) = 2.1 \text{ eV} \), \( G^1(pd) = 1.8 \text{ eV} \), and \( G^3(pd) = 1.0 \text{ eV} \), and the 4d spin-orbit splitting is 0.146 eV. Each calculated spectrum is labeled with the value of the Slater integrals in percent (\%) of the atomic values. In the extreme case that the Slater integrals are reduced to zero, i.e., neglecting the \( g(i,j) \) term (bottom-most spectrum in the right panel of Fig. 3), the peak A observed in experiment at the low-energy side of the L_2 XAS spectrum for Ru 4d^4 is absent, and the CFMC approach arrives at the same result as the single-particle model shown in Fig. 1. Thus it is clear that in the absence of the two-electron Coulomb interaction, the 4d spin-orbit coupling results in the closing of the t_{2g} channel at the L_2 edge for the 4d^4 configuration. However, as the Slater integrals are switched on, the t_{2g} channel at the L_2 edge becomes allowed and its intensity increases with increasing Slater integrals, while the t_{2g}-related spectral weight at the L_3 edge decreases. This means that for the L_2 edge in 4d^4 systems the 4d spin-orbit coupling suppresses the t_{2g}-related intensity, while the Slater integrals result in an intensity transfer from the \( \epsilon_g \) to t_{2g}-related peak. The combination of the 4d spin-orbit coupling and the Slater integrals thus results in a weak t_{2g}-related peak at the L_2 edge. Comparison
MULTIPLET EFFECTS IN Ru $L_{2,3}$ X-RAY-...  

of the data of Figs. 2 and 3 (right panel) gives best agreement for RuO$_2$ and Sr$_2$RuO$_4$ with the Slater integrals at about 40% of their atomic value. A further increase of the Slater integrals results in the overestimation of the multiplet effects, leading to unrealistically broad theoretical spectra. As can be seen at the top of Fig. 3 (right panel), for the highest Slater integral values considered, the degeneracy of the $t_{2g}$ and $e_g$ states is lifted, resulting in a triple-peaked structure. These values of the Slater integrals are reasonable in the light of a previous study of Nb(V), Mo(VI), and Ru(III) systems with $L_{2,3}$ XAS. 

The theoretical spectra for the 4$d^3$ configuration are shown in the left panel of Fig. 3 using 10$Dq = 2.7$ eV. In this case the $L_2$ edge has been shifted and multiplied by 2.6 for comparison. Since the covalency increases with increasing Ru valence, the Slater integrals have to be drastically reduced to as little as 15% of their atomic values in order to reproduce the experimental spectrum of Sr$_2$Ru$_2$O$_8$ as regards the intensity ratio $I(t_{2g})/I(e_g)$ and the energy shift with respect to the Ru(IV) compounds. However, importantly, the Slater integrals are not zero. On reduction of the Slater integrals to 0%, the relative intensity ratio of $I(t_{2g})/I(e_g)$ is larger at $L_3$ than $L_2$ giving again the same results as the single-particle scenario sketched in Fig. 1. An approximately equal $I(t_{2g})/I(e_g)$ ratio at the $L_2$ and the $L_3$ is found for a reduction to 10%. The extent to which the Slater integrals need to be reduced is larger for the 4$d$ than for the 3$d$ TM elements due to the more delocalized nature of the 4$d$ electronic states. As in the 4$d^4$ case, overly large Slater integrals (for 4$d^3$ meaning $>$20%) lead to the multiplet-induced breakdown of the crystal-field terms $t_{2g}$ and $e_g$, and, consequently, a triple-peak structure is clearly observed for the both $L_2$ and $L_3$ edges.

In the foregoing we discussed that the Slater integrals have little influence on the $L_3:L_2$ ratio, while the 4$d$ spin-orbit coupling has a large effect on it. In increasing the value of $L\cdot S(4d)$ only slightly from 0 to 0.14 eV, the $L_3:L_2$ ratio increases significantly from 2:1 to 3:1. The experimental $L_3:L_2$ ratio is 2.15:1 for both Ru(IV) compounds and is close to 2:1 for the Ru(V) system. This is assigned in the latter case to the quenching of the orbital moment due to the strong covalency. Further work is needed to understand the influence of the individual parameters, $L\cdot S(4d)$, 4$d$-4$d$ coupling (Slater integrals), 10$Dq$ (4D for tetragonal distortion) as well as the role of ligand hole 4$d^{n+1}L$ configuration, on the detailed spectral shape. Here we wish to stress that not only the 4$d$ spin-orbit coupling, but also the Slater integrals determine the details of spectral structure at the both the $L_2$ and the $L_3$ edges.

We now finish the paper with the presentation and discussion of the O-K XAS spectra for the same Ru (IV) and Ru(V) systems. In O-K XAS spectra, the correlation effects are much weaker than in the TM-$L_{2,3}$ XAS spectra, and meaningful comparison between the former and the results of band-structure calculations is plausible. Therefore, O-K XAS spectra are usually studied in order to explore the number and location of O 2$p$ holes induced by covalence or doping, and the crystal-field splitting in the ground state. Figure 4 shows the O-K XAS spectra of the three Ru oxides under consideration. The spectral structures just above the absorption edge are assigned to unoccupied O 2$p$ states caused by TM-4$d$O-2$p$ covalency. For RuO$_2$, the first peak, $A$, located at 529 eV, is assigned to states hybridized with a $t_{2g}$-related band, whereas the second peak, $B$, centered at ca 532 eV, is related to an $e_g$-derived band. This allows the derivation of the energy separation between the unoccupied portion of the $t_{2g}$ states to the $e_g$ states to be ca 3 eV, which is consistent with the results of band-structure calculations.

In the case of Sr$_2$RuO$_4$, a similar assignment of the O-K XAS spectra can be made. However, care should be taken, as band-structure calculations indicate that in the energy region 532–538 eV significant hybridization between O 2$p$ and Sr 5$d$ related states occurs. This has the consequence that the strong feature $C^*$ at 533.2 eV cannot be assigned to transitions into O 2$p$ orbitals hybridized with the $e_g$-related states alone, as was suggested recently.

As it possess the same O$_h$ symmetry, the spectral features of Sr$_2$Ru$_2$O$_8$ near the O-K threshold shown at the top of Fig. 4 are very similar to those in RuO$_2$, except for a shift to lower energy of ca. 1 eV, consistent with the observation of the 3$d$ transition-metal oxides. The shift of the Ru 4$d$-related states to lower energy results in a clear separation between the hybridized O 2$p$/Ru 4$d$ states and the states due to hybridization with Sr 5$d$, denoted $C$ in Sr$_2$Ru$_2$O$_8$; therefore, unlike Sr$_2$RuO$_4$, one can directly observe the $e_g$-related states in Sr$_2$Ru$_2$O$_8$. The energy separation between the unoccupied portion of the $t_{2g}$ states and the $e_g$ states in the Ru(V) system is ca 2.6 eV.

V. CONCLUSIONS

The correlation effects in the $L_{2,3}$ XAS spectra of 4$d$ TM compounds are not as strong as those of 3$d$ TM compounds, and therefore the observed spectral features in the case of O$_h$
symmetry reflect basically the $t_{2g}$ and the $e_g$-related unoccupied electronic states. However, we show here that the correlation effects do modify significantly the spectral intensity distribution, resulting in a difference between the $L_2$ and the $L_3$ spectra.

For Ru(IV) compounds, the 4$d$ spin-orbit coupling alone results in a zero transition matrix element to the $t_{2g}$-related states at the $L_2$ edge, while the Slater integrals result in intensity transfer from the $e_g$ to $t_{2g}$ related peak. The combination of both the 4$d$ spin-orbit and correlation interactions is shown to be responsible for the observation of a distinct but weaker $t_{2g}$-related peak at the $L_2$ edge than at the $L_3$ edge for two representative Ru(IV) systems RuO$_2$ and Sr$_2$RuO$_4$. For the Ru(V) compound Sr$_2$Ru$_2$O$_9$, this combination of effects results in an intensity ratio $I(t_{2g})/I(e_g)$, which is stronger at the $L_2$ than the $L_3$ edge. The reverse would be expected from the effect of the 4$d$ spin-orbit interaction alone. These observations indicate that the different $L_3$ and $L_2$ XAS spectral features in 4$d$ systems are not only due to 4$d$ spin-orbit coupling, but also to the effect of electronic correlation described by the Slater integrals.

Investigation of the three Ru compounds at the O-K edge revealed the following. The observed energy separation between the unoccupied $t_{2g}$ states and the $e_g$ states for RuO$_2$ of ca. 3 eV is compatible with the crystal-field splitting derived from band-structure calculations. For Sr$_2$RuO$_4$ no such conclusion is possible from the O-K XAS data due to the contributions from O 2$p$/Sr $5d$ hybrid states in the same energy region as the O 2$p$/Ru 4$d(e_g)$ states. For the Ru(V) system Sr$_4$Ru$_2$O$_9$, the features derived from O 2$p$/Ru 4$d$ hybrid states are shifted by some 1 eV to lower energy. This results in a clear separation between the O 2$p$/Ru 4$d(e_g)$ and O 2$p$/Sr $5d$ states. On going from Ru(IV) to Ru(V), both this shift to lower energy in the O-K edges and the observed shift to higher energy of the double peaks in the Ru-$L_{2,3}$ spectra follow the same pattern as is observed in the 3$d$ TM oxides.

Finally, the experimental and theoretical results here set up a reference for the more complicated $R_{2-x}$Ce$_x$Ru$_2$Cu$_3$O$_{10}$ systems in which both magnetism and superconductivity coexist.

ACKNOWLEDGMENTS

Z.H. thanks the DFG for financial support within the framework of the TU-Dresden’s Graduiertenkolleg ‘‘Struktur und Korrelationseffekte im Festkörper.’’ The research of F.d.G. was made possible by the Royal Netherlands Academy of Arts and Sciences (KNAW). We thank Professor Dr. J. Darriet and Dr. F. Grasset at the ICMCB, Bordeaux, for kindly providing the Sr$_2$Ru$_2$O$_9$ sample and HASYLAB for allocating beamtime.