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ABSTRACT

We present the 1s X-ray photoemission spectrum of α -Fe₂O₃ in comparison with its 2p photoemission spectrum. We show that in case of transition metal oxides, because the 1s core hole is not affected by core hole spin-orbit coupling and almost not affected by core-valence multiplet effects, the Fe 1s spectrum and the complementary charge transfer multiplet calculations allow for an accurate determination of the charge transfer parameters. The consistency of the obtained parameters for the 1s photoemission was confirmed with 2p photoemission calculations and compared to 2p experimental photoemission spectra.

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1. Introduction

Hard X-ray photoemission (HAXPES), a technique with broad possibilities for studies of complex materials and buried-layer nanostructures, is photoemission with excitation energies ranging from ~ 1.5 keV to more than 10 keV [1]. Due to the increased electron inelastic mean free paths of the photoelectrons using these large excitation energies, it is possible to apply photoemission to probe “true” bulk composition, atomic structure and electronic structure, as well as depth profiling for many systems of interest ranging from single compounds to multilayer nanostructures. In addition to the possibility of measuring more bulk-sensitive spectra for buried regions and interfaces, HAXPES allows to promote the emission of photoelectrons from core levels deeper than those usually accessible with conventional soft X-ray sources.

In particular for 3d transition metal (TMs) elements the common choice for photoemission studies concern mostly the 2p and 3s core level spectra, whose binding energies are in between 400 and 1000 eV, are easily accessible by employing quasi-monochromatic radiation provided by X-ray laboratory (Mg K α and Al K α at

1253.4 eV and 1486.3 eV, respectively) or synchrotron radiation sources to access the whole soft X-ray range. The 2p or 3s core level wavefunction overlaps strongly with the 3d states and make these 2p and 3s spectra sensitive to the electronic and magnetic structure of the probed elements [2] and in many cases the interpretation of the spectra has been well-established using the charge transfer multiplet model [3–6].

However, using synchrotron radiation with energy larger than 1.5 keV or a X-ray source equipped with Cu, Ti or Cr anodes [7–9], deeper core levels of the TMs can be studied, concerning in particular the measurement of the photoelectron emission from 1s levels and the Auger transitions associated with the formation of a 1s core hole [10–12]. HAXPES of 1s core levels was performed just for a few systems concerning iron metal and other 3d transition metals before, using a Cu K α_1 source [7,13], and on Ti metal and TiO₂ [14,15] or using synchrotron radiation on Ni metal [16] and nickel oxide [17] and Mn 1s photoemission of MnAs and Bi_{1.91}Mn_{0.09}Te [18]. Apart for these sparse measurements, no specific attempt focusing explicitly on the amount of information that could be obtained through the theoretical analysis of 1s core level spectra of TMs compounds has been performed up to now. To this purpose, here we present the study of the Fe 1s HAXPES spectrum for α -Fe₂O₃.

The 1s photoemission structure of Fe₂O₃ is expected to possess a relatively simple spectral shape due to the absence of core spin-orbit splitting and due to negligible 1s exchange splitting due to the small overlap between 1s and unfilled 3d orbitals [4]. Also the relative binding energy differences between different oxidation states

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are expected to be larger, allowing more straightforward oxidation state determination. This implies that the Fe 1s spectrum is not affected by core hole spin-orbit coupling and also it is not affected by core hole–valence multiplet effects, in contrast to the 2p photoemission spectral shape. Although these multiplet effects are useful for symmetry and spin determination in X-ray absorption [5,19], they complicate the detailed analysis of 2p, 3s and 3p photoemission spectra with regard to charge transfer parameters. In other words, the 1s metal spectra might turn out to be ideal spectra for the determination of the charge transfer parameters without the complications of additional effects. In addition, the charge transfer parameters determined from 1s photoemission, might serve well in resonant Auger analysis. The consistency of this analysis is confirmed through the good agreement occurring for calculating also the Fe 2p spectrum with the same values of the charge transfer parameters. To our knowledge Fe 1s photoemission has not been applied on iron oxides before and in addition, the 1s photoemission have not been calculated quantitatively before.

2. Experiment

Hard X-ray photoemission spectroscopy was performed on an α -Fe₂O₃ single crystal with photon energies of 10 keV and 7.7 keV for the Fe 1s and the Fe 2p spectra respectively. No surface preparation was performed prior to the experiment. The incidence angle of the X-ray beam was set at 45 degrees, while the emitted photoelectrons were collected at normal emission geometry. According to the Tanuma Powell and Penn algorithm (TPP-2M) formula [20,21] the inelastic electron mean free path (IMFP) for the 2p (1s) photoemission experiments with kinetic energy of about 7 (2.9) keV is 9.5 (4.6) nm. Accordingly, the information depth, roughly estimated as three times the IMFP was about 30 nm and 13 nm for the Fe 2p photoemission and Fe 1s photoemission, respectively, thus ensuring the bulk sensitivity typical of HAXPES measurements. The experiments were performed with the VOLPE spectrometer on beamline ID16 of ESRF [22,23], with an overall resolution of 0.48 eV at 10 keV and 0.42 eV at 7.7 keV. The energy scale is aligned on the Fermi energy or the 3d core level of a gold foil. All the measurements on the sample were collected at room temperature.

3. Theory

The photoemission spectra were calculated using the charge transfer multiplet program [5], in which a number of correlated ionic configurations together generate the ground state. The charge transfer multiplet program is based on Cowan's atomic code [24] and extended by Theo Thole et al. to implement symmetry [25] and charge transfer [5,26,27]. We limited the number of ionic configurations to three and describe the ground state of α -Fe₂O₃ with respectively EG1 = 3d⁵, EG2 = 3d⁶ \underline{L} and EG3 = 3d⁷ $\underline{L}\underline{L}'$, where \underline{L} indicates an oxygen 2p hole. Note that this means that the iron system is described by some combination of the three ionic configurations based on the energy differences, with detailed description below, between these three configurations. The energies of these three ionic states depend on the charge transfer parameters Δ , U and Q as shown in Fig. 1. These parameters have the following physical meaning: Δ is the charge transfer energy related to the energy difference between 3d⁵ and 3d⁶ \underline{L} . U is the Hubbard U parameter, the 3d–3d Coulomb interaction potential and identifies with the energy difference of 3d^{*n*} + 3d^{*n*} and 3d^{*n*–1} + 3d^{*n*+1}. Q is the core hole potential. We assumed that the core hole potential is the same for the 1s and the 2p core holes.

Although we only implemented three ionic configurations, we show the fourth ionic configuration as well in Fig. 1, in order to point out how much higher in energy this fourth configuration in both the initial and final state (EG4 and EF4) would be. In general, the relative energy of EG4 and EF4 shows that this fourth configuration can often be neglected.

The mixing of the ionic configurations through the interaction with the oxygen ligands was done with so-called hopping matrices T . This is an interaction of the 3d states with a ligand p state, meaning that the hopping matrices are interactions between the oxygen ligand 2p state and the different e_g and t_{2g} 3d-states of the iron in octahedral symmetry. We use $T_{e_g} = 2 * T_{t_{2g}}$ in our calculations [28]. Thus, effectively these hopping matrices T_{e_g} and $T_{t_{2g}}$ allow the interaction of the different ionic configurations with each other.

In addition to the fact that three ionic configurations were mixed, we simulated octahedral symmetry with a semi-empirical chosen crystal field energy (10Dq) of 1.9 eV and for all the three

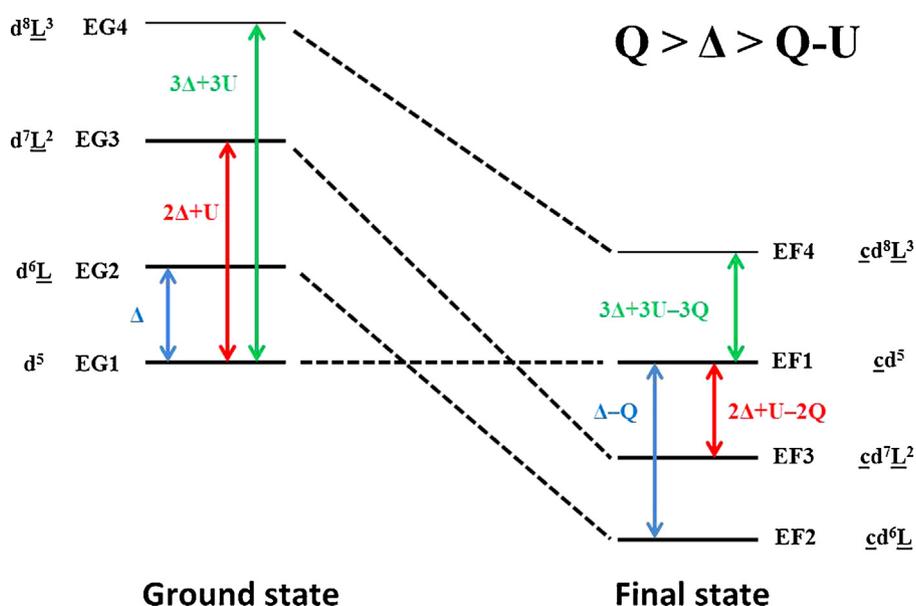


Fig. 1. Schematic representation of the ground states EG1, EG2, EG3 and EG4 on the left and the final states EF1, EF2, EF3 and EF4 on the right with the dependence of the relative energy of these states on Δ , U and Q . The order of the EG1, EG2, EG3 EG4 and EF4, EF3, EF2 and EF1 may change depending on the choice of the charge transfer parameters, but the present order validity is stressed with the equation at the right top.

separate configurations, electron correlations are taken into account with the Slater integrals F^{dd} and F^{sd} and G^{sd} (for 1s photoemission, for 2p photoemission the last two are F^{pd} and G^{pd}). The Hartree–Fock calculated Slater integral values are reduced to 85% to overcome Hartree–Fock errors and to compensate slightly for covalence [5]. We note that the F^{dd} for 1s photoemission and 2p photoemission is the same, while both F^{sd} and G^{sd} are orders of magnitude smaller than the F^{pd} and G^{pd} respectively, signifying that the 1s photoemission is not perturbed much by multiplet interactions.

The results of the charge transfer multiplet calculations, the calculated transition energies and the corresponding oscillator strengths (sticks) were broadened with a Lorentzian and a Gaussian to account for the life time broadening and experimental resolution respectively.

4. Results and discussion

Fig. 2 shows the experimental Fe 2p (A) and 1s (B) HAXPES spectra of α - Fe_2O_3 . The 2p HAXPES spectrum shows two main peaks split by the 2p spin-orbit coupling indicated with $2p_{3/2}$ and $2p_{1/2}$ respectively plus two clear satellite structures S and S' that have been assigned to charge transfer excitations. The relative energies of S, $2p_{1/2}$ and S' relative to $2p_{3/2}$ are 8.37, 13.76 and 22.5 eV respectively. In the following we compare the Fe 2p photoemission spectrum with reference literature, but first we have a look at the Fe 1s HAXPES. The excitation of a 1s electron implies that the final state is not affected by spin-orbit coupling and also not by strong core-hole

induced multiplet effects, however the 1s photoemission spectrum shown in Fig. 2B shows three peaks named 1s, S1 and S2 where S1 and S2 are mainly due to charge transfer effects, as will be analyzed below. The relative energy of S1 and S2 to the main 1s peak is 8.57 and 16.56 eV respectively. Note that the Fe 1s HAXPES spectrum shown in Fig. 2B is the first Fe 1s spectrum of Fe_2O_3 to our knowledge.

We continue with the analysis of the more common 2p photoemission, since there are charge transfer parameters known for simulation of the spectrum and as well there are reference spectra available. The Fe 2p photoemission spectrum of Fe_2O_3 has been studied before in combination with detailed multiplet analysis [29–31]. Fujii et al. have shown an Fe_2O_3 photoemission spectrum combined with a charge transfer multiplet calculation using two configurations (Fe^{3+} , d^5 and d^6L) with $\Delta = 2$ eV, $T_{eg} = 2.6$ ($Tt_{2g} = 1.3$), $U = 7.5$ eV and $Q = 8.0$ eV and a crystal field energy of $10Dq = 0.5$ eV [31] (see also Table 1). Their crystal field value $10Dq$ of 0.5 eV is (too) low for Fe^{3+} and a value of $10Dq$ of approximately 1.5 eV would be more in line with 2p X-ray absorption analysis [5,32], but we note that the exact value of $10Dq$ is less important for the shape of the 2p photoemission spectrum that is dominated by 2p spin-orbit coupling and charge transfer effects. We use these Fujii et al. charge transfer parameters, defined as set B, as a starting point for our fits. It has been found that simulations improve if three electronic configurations are used for the simulation of 2p photoemission spectra [33].

Our Fe 2p HAXPES spectrum resembles the soft X-ray 2p X-ray photoemission of Fe_2O_3 from literature [29,31,34–36] as can be confirmed from Fig. 3A in comparison to two reference spectra [31,34]. The differences between the reference experimental 2p photoemission spectra of Fujii et al. [31] and Droubay et al. [34] are in the 708–710 eV binding energy (BE) region. The double-peak-like pattern in this region of the photoemission measured at normal emission (90°) published by Droubay et al. is different from the observation of a single broader peak with a shoulder at lower BE in the spectrum of Fujii et al. [31]. This difference was ascribed to the difference in geometric and electronic structure of the Fe at the surface relative to the bulk [34]. In short, since there is a bulk contribution with different symmetry than the surface (with lower symmetry), there is a slight energy difference between the two components. In the bulk 2p HAXPES spectrum measured by us also two contributions at the main peak at 710 eV binding energy are encountered (Fig. 3A, black line): the peak at lower BE is attributed to surface related photoemission and the lower

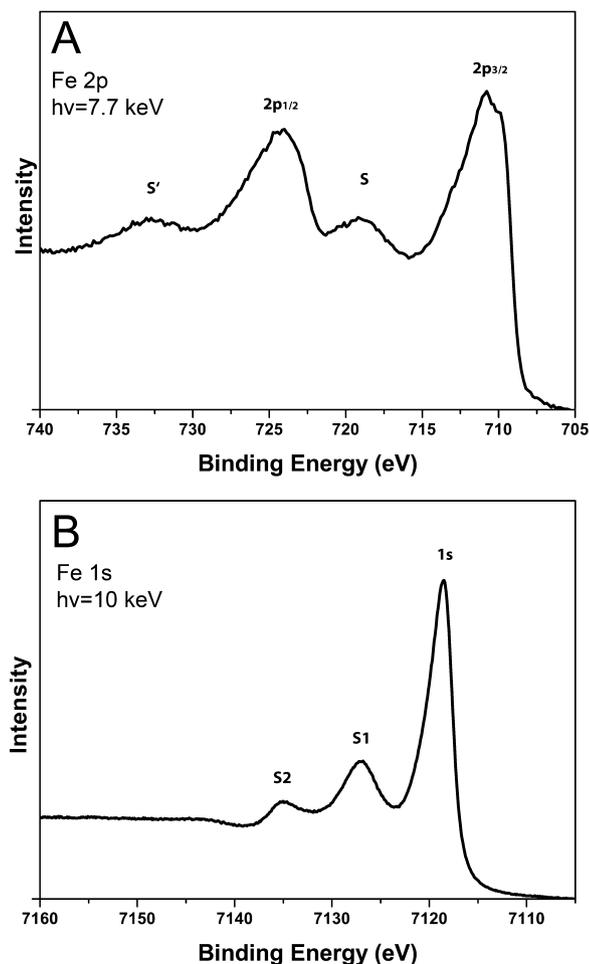


Fig. 2. Fe 2p (A) and Fe 1s (B) HAXPES spectra of α - Fe_2O_3 .

Table 1

Energy of the ground states (EG1, EG2 and EG3) and final states (EF1, EF2, EF3) for two sets A and B of Δ , U and Q for analysis of Fe_2O_3 . The relative ground state contributions (% EG1, %EG2 and %EG3) in the photoemission calculation are presented as well.

Set	A	B [31]
Δ	3.0	2.0
U	7.5	7.5
Q	9.0	8.0
EG1	0	0
EG2	3.0	2.0
EG3	13.5	11.5
EG4	31.5	28.5
$10Dq$	1.9	0.5
EF1	0	0
EF2	-6.0	-6.0
EF3	-4.5	-4.5
EF4	4.5	4.5
% EG1	54.1	48.3
% EG2	41.7	46.6
% EG3	4.2	5.1
T_{eg}	2.7	2.6
Tt_{2g}	1.35	1.3

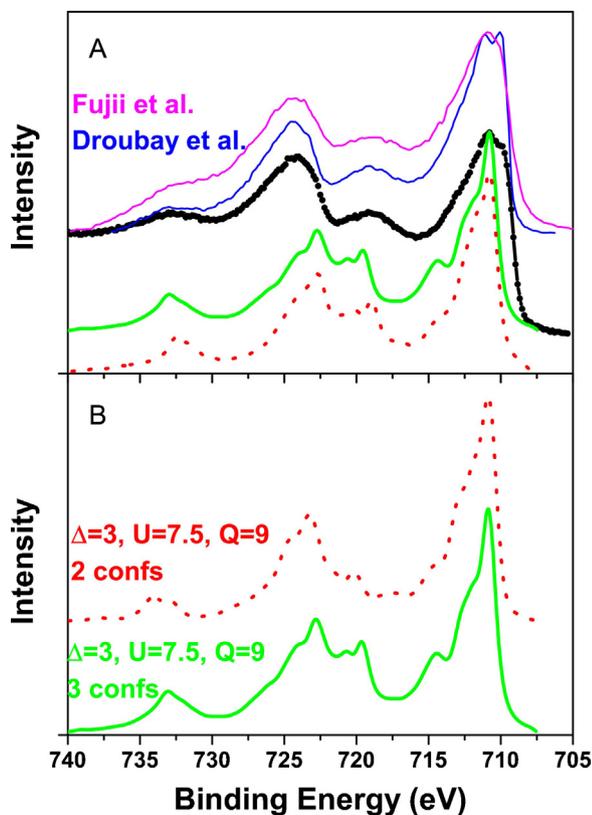


Fig. 3. (A) Experimental Fe 2p photoemission of α -Fe₂O₃ versus binding energy (black) compared with charge transfer multiplet calculations using charge transfer parameter set B [31] (red dotted) and set A (green solid). For comparison two reference 2p photoemission spectra as published by Fujii et al. [31] (pink) and Droubay et al. [34] (blue) are shown at the top. (B) Fe 2p photoemission charge transfer multiplet calculations with only one set of charge transfer parameters (set A, Table 1) with either three configurations (green solid, same as in panel A) or with two configurations (red dotted). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

symmetry at the surface is not taken into account in our multiplet calculations, which is the reason why the calculations do not entirely agree on this BE feature at 710 eV.

The Fe 2p photoemission simulations using our optimized charge transfer parameter sets A ($\Delta=3$, $U=7.5$ and $Q=9.0$ and $10Dq=1.9$ eV, Table 1) and B (from Fujii et al. [31], Table 1) are also compared with our Fe 2p HAXPES in Fig. 3A. The corresponding energies of the ground and final states of the parameter sets are written in Table 1 and show that the parameter set B as used by Fujii et al. [31] and our optimized parameter set A have the same final state (EF1, EF2, EF3 and EF4) energies. Note that these relative state energies do not directly have a reference to the energy distances between peaks; compare for example with the relative energies of $2p_{1/2}$, S and S' (8.37, 13.76 and 22.5 eV) to $2p_{3/2}$. We also point out that the obtained parameters for Δ and U of both set A and B relate well to estimates of Bocquet et al. for Fe³⁺ compounds [37]. The parameter set A and B differ in the fraction of the different states contributing to the ground state. For parameter set A, the contribution of the $3d^5$ ionic state is increased.

Fig. 3B shows the difference between charge transfer multiplet calculations with three and two configurations using the charge transfer parameter set A. The relatively small difference between the Fe 2p photoemission calculations with two or three configurations can be attributed to (i) the contribution of the third configuration is relatively small compared to the first two configurations and (ii) the third configuration in the $2p_{3/2}$ photoemission

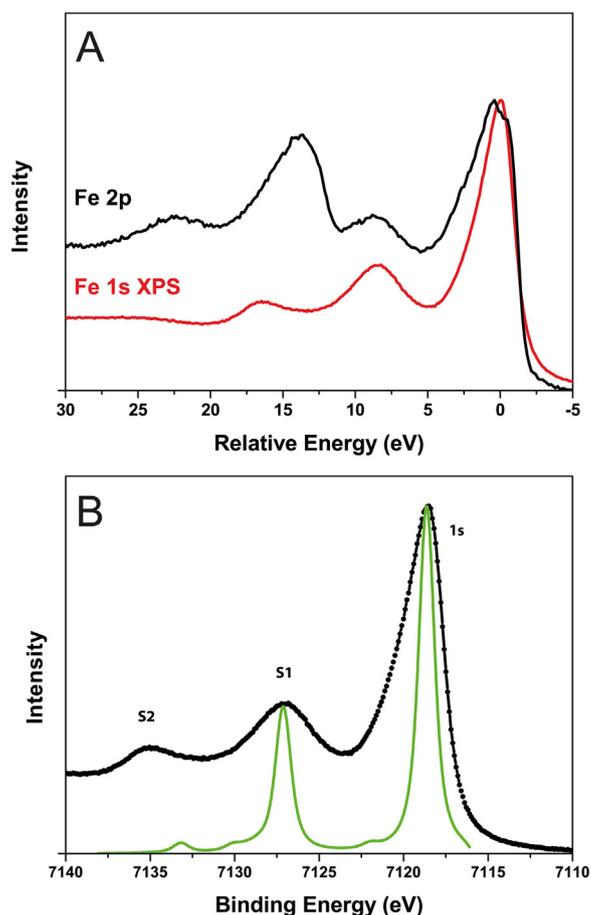


Fig. 4. (A) Experimental Fe 2p HAXPES (black) and Fe 1s HAXPES of α -Fe₂O₃. The main Fe 1s photoemission (red) and 2p photoemission (black) peak is shifted to zero. (B) Experimental Fe 1s HAXPES versus binding energy for α -Fe₂O₃ (black) compared with charge transfer multiplet calculations using parameter set A (green solid). The charge transfer multiplet calculation was performed with 85% of the Hartree-Fock Slater integrals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

will end up at about the $2p_{1/2}$ photoemission edge of the first configuration.

Fig. 4A shows the experimental Fe 2p HAXPES and the binding energy shifted Fe 1s HAXPES of Fe₂O₃. The experimental Fe 1s HAXPES shows three peaks. As mentioned above, on itself the creation of a photoelectron from the 1s level should only give rise to a single peak, while the observation of three peaks suggests that at least three different states are contributing to the ground and final state of the process, namely the formal valence $3d^5$ (Fe³⁺) and two additional states.

As displayed in Fig. 3B, it is not obvious from the Fe 2p photoemission that one should take into account three configurations, since the third configuration of $2p_{3/2}$ ends up below the $2p_{1/2}$ edge of the first configuration. Grosvenor et al. showed a multi-peak fitting of Fe 2p photoemission of Fe₂O₃ with three contributions and an extra surface contribution taken into account [30]. Three-state analysis was applied before on the 2p photoemission of the nickel and cobalt halides as well [33]. The comparison of Fe 1s HAXPES with 2p HAXPES in Fig. 4A shows that $2p_{3d}$ multiplet effects and spin-orbit splitting disallow a direct observation in Fe 2p photoemission that two or three ionic configurations need to be taken into account, while it becomes clear directly from the Fe 1s HAXPES spectrum. This also means that it is very well possible that in many cases, where Fe 2p photoemission is analyzed in terms of charge

transfer multiplet parameters, extra required configurations have been neglected.

Fig. 4B shows the comparison of the 1s experimental HAXPES with the calculated photoemission using charge transfer parameter set A. No background was subtracted from the experimental 1s photoemission, which would lead to a substantial lower peak at 7135 eV in the experimental spectrum. In addition, possibly a fourth configuration is required for the calculation in order to obtain an increase of the intensity of the peak at 7135 eV. This consideration is based on the relative energy difference between the EF4 and EF2 state (Table 1) that is around 10.5 eV. Note that both parameter set A and B show very similar Fe 1s photoemission, but for parameter set A, the one that is shown in Fig. 4B, the peak around 7127 eV agrees slightly better with the energy of the experimentally observed peak in this range and the feature at lowest BE is at slightly lower energy for the third band at 7135 eV compared to parameter set B.

The charge transfer multiplet program uses Δ , U and Q , which we have made general for 1s and 2p photoemission. Especially for Δ and U this is logical, since there is no difference between U in 1s or 2p photoemission, since U comes from 3d–3d interaction and there is no reason to assume that the relative energies of the ionic configurations, determined by Δ and U in the initial state would be different for 2p and 1s photoemission. In addition, we assumed that the core hole potential is the same for a 2p and 1s hole, which leads to the same Q in simulations of 2p and 1s photoemission.

In reference [16] Karis et al. reported that the 3d shake-up for Ni metal is found at different relative energies for the 1s photoemission (4 eV) and the $2p_{3/2}$ photoemission (6 eV) compared to the main photoemission line. We claimed above that Δ , U and Q can be taken general for 1s and 2p photoemission. In addition, we want to point out that as well the energies of the different configurations in the ground state (EGx) and the crystal field 10Dq do not depend on the core hole (either 1s and 2p) created in the same sample (but depend on the sample). Following this reasoning, the energies of the configurations in the final state (EFx) could also not be responsible for the observation in [16] since those depend directly on the Δ , U and Q . Because the direct and exchange Coulomb interactions between 2p and 3d electrons are much stronger than between 1s and 3d electrons and (in addition there is a 2p core hole splitting compared to no splitting for 1s core holes) and because of this difference in electron interaction strength, we believe that different relative energies of shake-up features compared to the main photoemission line can be expected. By coincidence the first shake-up for Fe 1s photoemission (8.57 eV) compared to Fe 2p photoemission (8.37 eV) of Fe_2O_3 is almost at the same relative energy, but this is not necessarily the case as was observed in [16]. Note that in their analysis, Karis et al. changed the value of Q (or $Q-\Delta$ as they mention) slightly and changed as well the U between 1s and 2p photoemission (where we believe U should not depend on the 1s or 2p hole). As well, while Karis et al. observe that the Fe $2p_{3/2}$ photoemission shake-up is at 6 eV, their simulation shows that there is a small contribution already at about 4 eV. It is just that the multiplets resulting from the $2p_{3/2}$ electron interaction lead to a higher intensity contribution at 6 eV. Another interesting observation they make is that the shake-up of $2p_{1/2}$ is at 4.6 eV, which is still a little bit higher than the shake-up of 1s photoemission. This would imply that the $2p_{1/2}$ 3d electron interaction is already much weaker than $2p_{3/2}$ 3d, an observation which fits well to features obtained in the L_3 versus L_2 edge of X-ray absorption [5,6,25].

In summary, one can conclude that 1s photoemission is the best reference experiment to perform to obtain the relevant charge transfer parameters. We point out that the extra ionic configurations are not of relevance for X-ray absorption analysis as has been pointed out before [38].

5. Summary and conclusions

We have shown both Fe 2p and 1s HAXPES of Fe_2O_3 . Although not mentioned before we would like to state that the presented charge transfer parameters obtained for Fe 2p and 1s HAXPES could also be applied on calculations of the Fe 3s and 3p photoemission. The values obtained from the calculated Fe 2p and 1s HAXPES of $\alpha\text{-Fe}_2\text{O}_3$ are in close agreement with values found for Fe 2p photoemission by Fujii et al. [31] and Bocquet et al. [37]. The Fe 1s HAXPES contains three distinct features and this directly implies that at least three configurations have to be taken into account in the charge transfer multiplet calculations of Fe photoemission of Fe_2O_3 . On the other hand, there is not a big difference between two and three configuration in the case of Fe 2p photoemission due to the multiplet and 2p spin orbit coupling complicating the direct observation of a third configuration. Overall, the Fe 1s HAXPES gives a more direct way to obtain the charge transfer parameters in the charge transfer multiplet photoemission calculations than Fe 2p photoemission and 1s HAXPES shows clearly the amount of states that have to be taken into consideration in theoretical treatment.

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