

Soft x-ray emission during excitation of higher lying thresholds

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INTRODUCTION

The *intraatomic* resonant photoemission [1] takes place *within* the atom and leads to a resonant enhancement in the photoemission intensity of an outer shell when the excitation energy can excite an electron of a deeper lying shell. Recently, the *interatomic* multi-atom resonant photoemission (MARPE) has been suggested, which involves a large number of atoms. First photoemission measurements of this effect in metal oxides have been reported [2] and a theoretical model has been developed to describe the effects [3]. MARPE occurs when photon energy is tuned to a core-level absorption edge of an atom (here Ti 2p) neighboring the emitting atom with the emitting level (here C 1s) having a lower binding energy than the resonant level. If existent, the effect should be sensitive to bonding distances, bonding type and magnetic order and would provide a direct way to determine near-neighbor atomic parameters. Therefore it would offer a broad variety of possible applications. Since the effect increases the number of core holes in the sample, the effect should be detectable via fluorescence or Auger decay. A recent study [4] presents experimental evidence for an enhanced decay of the primary core hole detected via fluorescence emission (from MnO) and Auger electron emission (from Fe₂O₃).

We studied this effect in X-ray fluorescence. We measured the excitation energy dependence of C K_α emission spectra of TiNbC for different angles near the Ti 2p thresholds and found no significant enhancement of the emitted intensity. Especially in consideration of the broad applicability of MARPE, soft x-ray fluorescence appears to be not a suitable technique to study such effects.

MEASUREMENTS

Our measurements were performed at Beamline 8.0.1 of the Advanced Light Source, Lawrence Berkeley Laboratory. The resolving power has been set to $E/\Delta E = 550$ for TiNbC. The emitted radiation is analyzed with a resolving power of the spectrometer of about 620 (at 280 eV). The angle between the incident beam and the spectrometer was fixed at 90°. The absorption spectra were taken in the sample current mode. The sample was a bulk of polycrystalline TiNbC. All experimental curves are displayed as measured without broadening or smoothing the data. In order to compare our measurements with a simple model that takes the re-absorption of the emitted fluorescence emission and allows to calculate the (partial) fluorescence emission from a certain transition while the excitation energy is tuned through a higher lying threshold of a different compound. The details are described in detail elsewhere [5]. In Fig. 1 the C K_α partial fluorescence yield for TiNbC is shown for 3 different angles of incidence (to the sample surface). The excitation energy is scanned through the Ti 2p edge. The detector window is narrowed to accept C K_α photons (265-284eV) only. Two minimums are observed which coincide with the Ti L₂ and L₃ thresholds. The C K_α fluorescence decreases by about 56 % (for $\alpha=15^\circ$) when the

excitation energy reaches the Ti L_2 threshold. The excitation energy is scanned through the Ti 2p edge. The detector window is narrowed to accept C K_α photons (265-284eV) only.

Two minimums are observed which coincide with the Ti L_2 and L_3 thresholds. The C K_α fluorescence decreases by about 56 % (for $\alpha=15^\circ$) when the excitation energy reaches the Ti L_2 threshold. The reason for the decrease in general is that less incoming photons create C 1s core holes because the photons are directed towards the opening Ti 2p channels. The dashed curve corresponds to the calculation of the partial fluorescence yield. In the insert the Ti 2p absorption as used for the calculation is shown and the extended absorption spectrum including the carbon K edge. The calculated curves match the measured curves in Fig. 1 fairly well. In particular the data do not show a larger fluorescence yield than the calculated curve and therefore do not indicate an increased number of C 1s holes due to a multi-atom resonant interaction. We therefore cannot conclude that the measured fluorescence yield shows a greater fluctuation than the calculated yield. The largest deviation

between measurement and calculation (at the Ti 2p peak) is about 3% in the sense that the measured fluorescence signal drops in the peak by 55% and the calculated signal by 58%. Although our measurements suggest that the MARPE effect should be at most a 3% effect, we find it difficult to obtain the correct peak to background ratio in the absorption with the same accuracy. It is not possible to conclude that the measured fluorescence is generally stronger than calculated which would indicate an increased number of C 1s core holes due to a multi-atom resonant effect. We confirmed these findings for LaF_3 [5]. Apparently the intensity of the calculated spectra increases more rapidly than the measured curves once the high-energy threshold is passed. It is presently unclear what could account for this behavior but that it could be due to increasing non-radiative processes like Auger emission. Crucial parameters for the calculation are the correct peak to background ratio in the measured absorption spectra and the same resolving power of the exciting radiation when obtaining the partial fluorescence and the electron yield absorption spectra. For example an increase in resolving power will result in an increase in the peak to background ratio of the absorption (and emission) spectrum, which ultimately enhances the contrast in the calculated curve. We have measured the absorption and the partial fluorescence emission spectra simultaneously. Due to the inherently low fluorescence yield count rates a moderate resolution has been chosen although the strong signal provided by the absorption measurement would allow for absorption spectra to be obtained at much higher resolution.

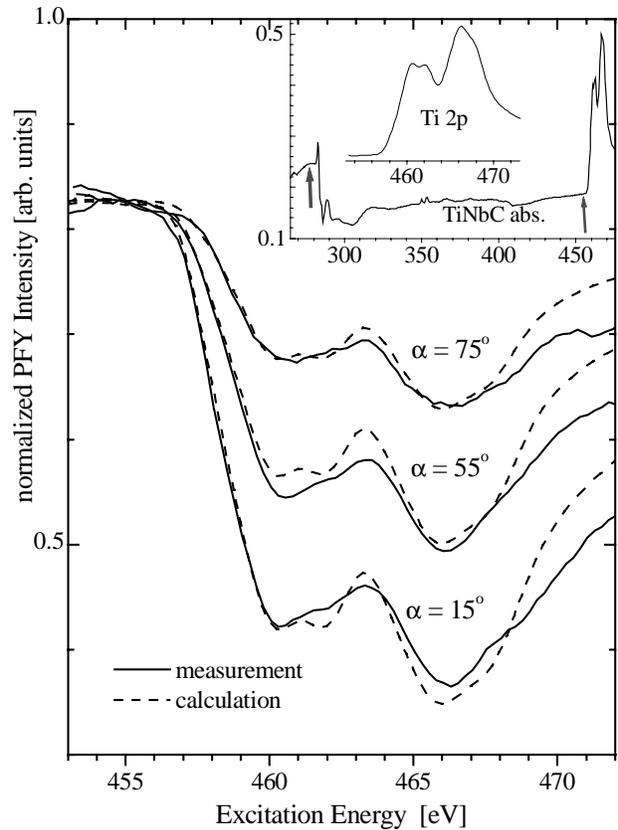


Figure 1: Carbon K_α partial fluorescence yield (solid line) and calculation (dashed line) for TiNbC. The excitation energy is scanned through the Ti 2p resonances. The XAS spectra across the Ti 2p threshold and the extended absorption across C 1s including Ti 2p threshold are shown in the

In most cases a clean surface (by photoemission standards) is not required for x-ray emission experiments because the escape depth of the fluorescence photons is large compared to the thickness of the adsorbates that form a layer in the order of 1 nm thick. Therefore most of the fluorescence arises from the bulk of the sample. For the absorption measurement surface contamination layers influence the spectrum more strongly due to the much smaller escape depth of the photoelectrons. Annealing of the TiNbC did not produce an enhancement in the peak to background ratio of the absorption spectrum.

To summarize, we have monitored the partial fluorescence ($C K_{\alpha}$ in TiNbC) of the carbon atoms while the excitation energy passes the higher threshold ($Ti 2p_{1/2,3/2}$) of the neighboring Ti-atoms. We do not find any evidence for an enhancement in the number of Carbon core holes produced by the multi-atom resonances and therefore no indication for the MARPE effect. Inherent difficulties such as the weak fluorescence signal and measurement of the correct peak to background ratio (clean sample, same resolving power for XES and XAS) lead us to the conclusion that fluorescence spectroscopy is not a suitable way to detect multi-atom resonances especially with regard to possible routine and broad applications.

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