A RIXS and DFT study of the novel Titanium Oxonitridophosphate $Ti_5P_{12}N_{24}O_2$

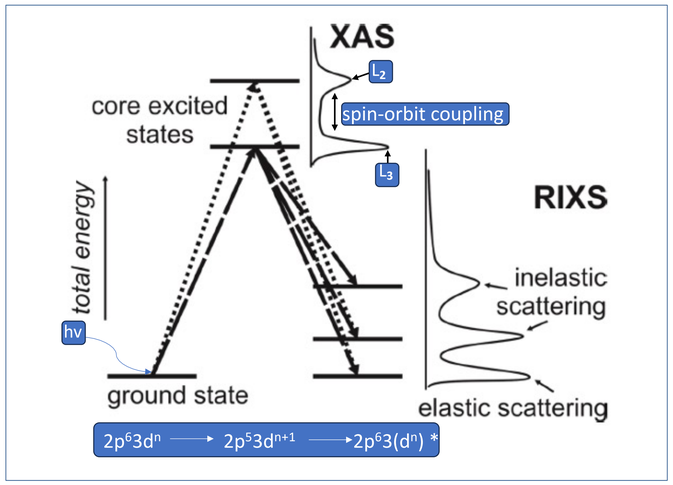
Peter Ufondu[1], Teak Boyko[2], Monika Pointner[3], Lucien Eisenburger[3], Schnick Wolfgang[3], Alexander Moewes [1]

1. University of Saskatchewan 2. Canadian Light Source, 3. University of Munich

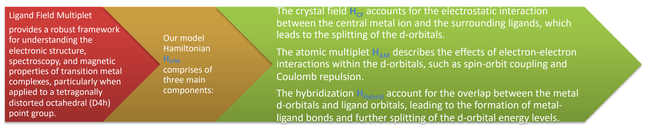
Introduction

Titanium Oxonitridophosphate (**$Ti_5P_{12}N_{24}O_2$**) is relatively new class of multinary materials obtained at high temperature (HT) and high pressure (HP) from binary TiN and P_3N_5 upon the addition of NH_4F as a mineralizer [1]. **$Ti_5P_{12}N_{24}O_2$** is experimentally confirmed to have an optical band gap of **1.6 eV** [1]. Regarding the reduced bandgap, **$Ti_5P_{12}N_{24}O_2$** shows promising properties for solar power harvesting and photocatalysis. In this study, we employ resonant inelastic X-ray scattering (RIXS). This technique directly probes electron dynamics and energy landscape to reveal the effect of symmetry distortion in the electronic structure of **$Ti_5P_{12}N_{24}O_2$**.

RIXS: Photon In Photon Out Experiment



RIXS: Theory



A higher order equation called **Krammers-Heisenberg** is used to account for the RIXS process [2]:

$$F(\Omega,\omega) = \sum_f \left| \sum_i \frac{\langle f|T_2|i\rangle\langle i|T_1|g\rangle}{E_g - E_i + \omega - i\Gamma_i/2} \right|^2 * \frac{\Gamma_f/2\pi}{(E_g - E_f + \Omega - \omega)^2 + \Gamma^2 f/4}.$$

Quanty is a scripting language that enables users to program and solve quantum mechanical problems in second quantization. [3-4].

Results

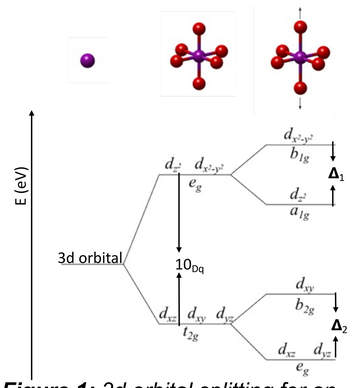


Figure 1: *3d orbital splitting for an Octahedral and distorted Octahedral symmetry.*

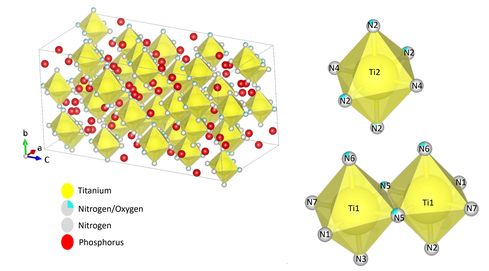


Figure 2: *Crystal Structure of $Ti_5P_{12}N_{24}O_2$*

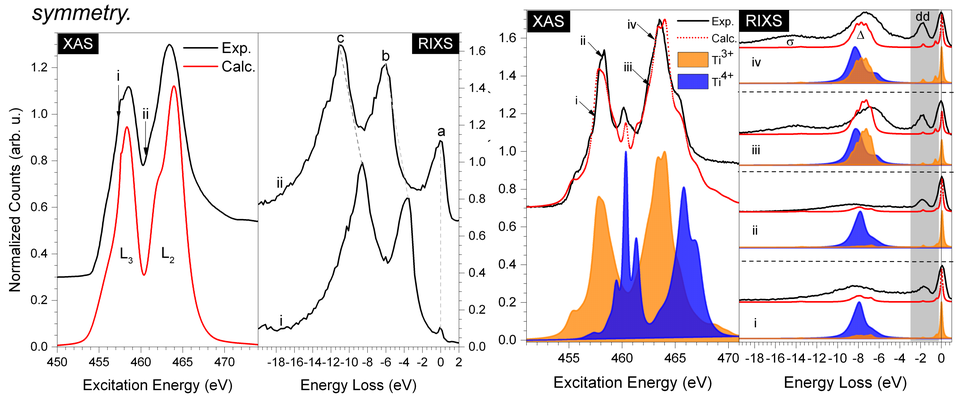


Figure 3: *Measured and calculated XAS and RIXS spectra (Left): Titanium Nitride (TiN) at the Titanium $L_{2,3}$-edges ; (Right): $Ti_5P_{12}N_{24}O_2$ at the Titanium $L_{2,3}$-edges.*

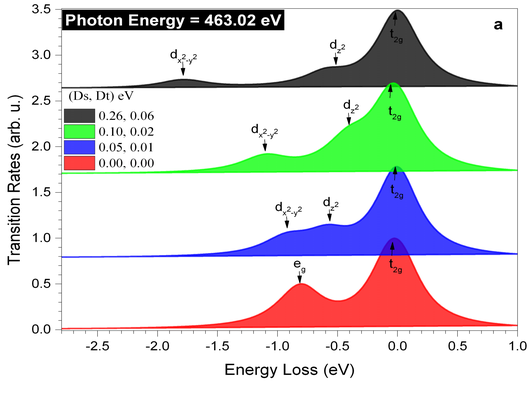


Figure 4: *Calculated RIXS spectra of $Ti_5P_{12}N_{24}O_2$ at the Titanium $L_{2,3}$-edges, showing the effect of distortion on the electronic structure.*

Parameter	$Ti_5P_{12}N_{24}O_2$		TiN
	Ti^{4+}	Ti^{3+}	Ti^{3+}
10_{Dq}	0.51	0.50	0.56
Ds	0.19	0.25	-0.95
Dt	0.13	0.05	0.05
ζ_{2p}	1.01	0.92	0.90
ζ_{3d}	1.01	0.90	0.96
F_{dd}	0.91	0.99	0.98
F_{pd}	0.99	0.91	0.99
G_{pd}	0.84	0.90	0.83
U_{dd}	4.83	4.51	3.36
U_{pd-dd}	1.15	4.99	4.99
10_{DqL}	0.53	0.47	0.99
Δ	2.77	1.87	2.57
Δ_1	1.49	1.30	1.76
Δ_2	0.50	0.03	0.92

Table 1: *The optimized electronic structure parameters used in this calculations for Ti^{3+} and Ti^{4+} ions in the $Ti_5P_{12}N_{24}O_2$ and TiN samples. The spin orbit coupling ζ_{2p}, ζ_{3d}, and Slater integral parameters F_{dd}, F_{pd} and G_{pd} are scaled by this dimensionless factors. The other parameters are in eV.*

Discussion

1. Our study presents the results of Ti $L_{2,3}$-edge X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) analysis of the novel Titanium Oxonitridophosphate $Ti_5P_{12}N_{24}O_2$.
2. There is good agreement between our calculations and the measured XAS and RIXS spectra.
3. The Ligand Field Multiplet Theory (LFMT) calculations employed to analyze the $2p^63d^n \rightarrow 2p^53d^{n+1} \rightarrow 2p^6(3d^{n*})$ transition in a tetragonal symmetry (D4h) shows that $Ti_5P_{12}N_{24}O_2$ contains two valence states of Titanium, (Ti^{3+} and Ti^{4+}), in the ratio of 0.9:0.1. This outcome is due to the Jahn-Teller distortion that arises from the overlapping wavefunctions of 2p electrons in the Nitrogen-doped ligand Oxygen and 3d electrons in the transition metal (Titanium).
4. The measured XAS spectrum looks like the Ti^{3+} TiN XAS but with an additional peak at 460 eV between the two prominent peaks.
5. Our calculations show that the peak at 460 eV is due to Ti^{4+} Titanium site present in the $Ti_5P_{12}N_{24}O_2$.
6. The RIXS spectra are dominated by d-d excitations with energy between 0.4 and 2.5 eV from the Ti^{3+} Titanium site.
7. Our calculations indicated that the first energy loss feature present in the RIXS spectra is not due to local spin flip but rather a distortion in the symmetry of the crystal resulting in the splitting of the e_g orbitals by an energy of approximately 1.3 eV.
8. The calculated values for Ds and Dt suggest that Ti^{4+} has a more distorted symmetry than Ti^{3+} in the crystal.

References

1. Eisenburger, L.; Weippert, V.; Oeckler, O.; Schnick, W. Chemistry – A European Journal 2021, 27, 14184–14188.4.
2. W. Kramers, H. A.and Heisenberg, Zeitschrift für Physik, vol. 122, pp. 681–708, 1925. English translation published in van der Waerden, sources of quantum Mechanics, 1967, op.cit., 223-252.
3. Y. Lu, M. Hoeppner, O. Gunnarsson, and M.W. Haverkort, Phys. Rev. B 90, 085102 (2014).
4. M.W. Haverkort, G. Sangiovanni, P. Hansmann, A. Toschi, Y. Lu, and S. Macke, Bands, resonances, Euro. Phys. Lett. 108, 57004 (2014).

Acknowledgement

We gratefully acknowledge the support and assistance from:
1. The department of Physics and Engineering Physics.
2. The Beamteam group.
3. The NSERC CREATE to INSPIRE.
4. The REIXS beamline at Canadian Light Source.
5. The Department of Chemistry University of Munich.

2nd Place Award Winning Poster at the 4th Engineering Graduate Research Conference.