



Contribution ID: 130

Type: Oral presentation

Mapping excitation-specific electron, spin and nuclear dynamics in spinel Co_3O_4 thin films with femtosecond X-ray emission spectroscopy and diffraction

Tuesday, 13 September 2022 12:00 (15 minutes)

We present a combined femtosecond X-ray emission spectroscopy (fs-XES) and X-ray diffraction (fs-XRD) study of spinel Co_3O_4 , a system representing a prototypical case of the intrinsic complexity of transition metal oxides, due to a correlated response of its nuclear, spin and electronic degrees of freedom.

This material has a normal spinel structure where Co^{2+} and Co^{3+} centres are surrounded by O^{2-} anions and respectively occupy tetrahedral and octahedral sites with a 1:2 stoichiometric ratio. As a consequence, the electronic configuration of the metal centres is characterized by paired and unpaired d-electrons, and it determines the presence of Mott-Hubbard and charge transfer gaps close in energy in the Visible-NIR range, making it promising candidate for photovoltaic and photocatalytic applications [1].

A full understanding of the material's photodynamics and the excitation wavelength influence on its photoreponse calls for investigation techniques able to follow the charge carrier relaxation with ultrafast time resolution and with electronic and nuclear sensitivity. Here we excite the ligand-to-metal charge transfer (LMCT, 400 nm) and metal-to-metal charge transfer (MMCT, 800 nm) transitions of 27 nm Co_3O_4 thin films simultaneously mapping the lattice response with fs-XRD, and the spin and electronic transient configurations of the Cobalt centres with fs-XES. The experiment was performed at the FXE instrument of the European XFEL facility probing the system in grazing incidence with a pink beam centred at 9.3 keV and detecting the XRD signal with the LPD detector and the nonresonant Co $K\alpha_{1,2}$ and $K\beta_{1,3}$ emission lines using a Von Hamos spectrometer and Jungfrau detectors.

Our joint investigation shows distinct decay pathways for the two excitation channels that are inaccessible with transient optical techniques. The results outline a radically different picture compared to previous time-resolved studies of Co_3O_4 [2], excluding a stepwise cascade mechanism in the charge carrier relaxation of the material and highlighting the relevance of electron-phonon coupling in the photocarrier response on ultrafast time scales [3].

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Session Classification: MS

Track Classification: Italy@EuXFEL