Microscopic investigation of photodoping in the charge transfer insulator NiO using time-resolved X-ray absorption spectroscopy at the European XFEL

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Motivation

Main Question: What influence do electronic correlations have during nonequilibrium dynamics in a charge-transfer insulator?

Scientific background:

- Electronic correlations play a large role in band formation and deciding between charge-transfer or Mott type behavior in insulators [1]
- Understanding role of electronic correlations during non-equilibrium dynamics could allow finetuning of material properties under optical excitation for specific applications

Synopsis:

- Disentangling modifications at the Ni L_3 (L_2) edge and investigating effects of electronic correlations using GW plus embedded dynamical mean field theory (GW+EDMFT) calculations
- Relating additional modifications to variations in the ground state using a multiplet model

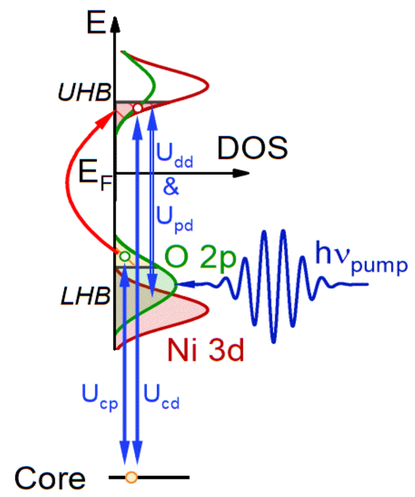

Figure 1: *Schematic representation of electronic correlations in an excited charge-transfer insulator*

Methode & Setup

Time-resolved X-ray Absorption Spectroscopy (tr-XAS) [2]:

- Element-specific study of the unoccupied electronic states in pump-probe scheme
  - Pump (optical laser): Excites electrons from the lower to the upper Hubbard band (LHB/UHB)
  - Probe after Δt (X-rays): Exciting core electrons into unoccupied electronic states

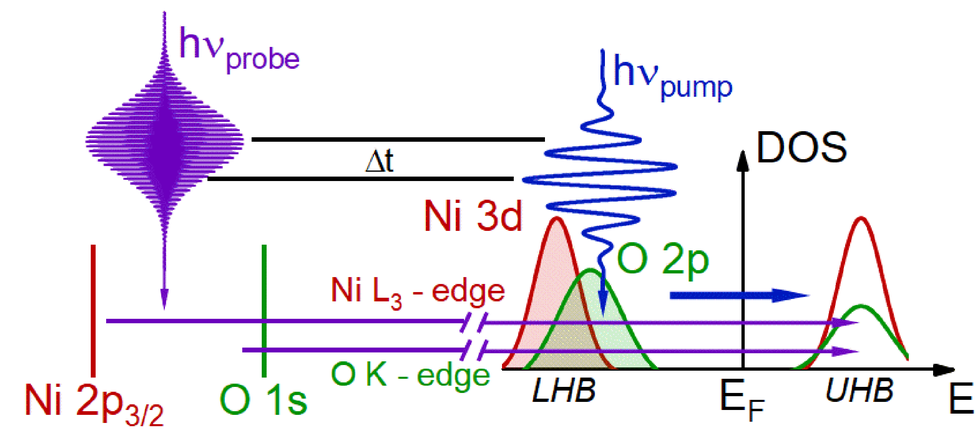

Figure 2: *Sketch of the time-resolved optical pump, x-ray absorption probe experiment at the Ni L_3 (2p3/2 → 3d) and O K (1s → 2p) absorption edge with time delay Δt. [3] (modified).*

Spectroscopy and Coherent Scattering (SCS) Instrument of the European XFEL [4,5,6,7]:

- Special transmission zone plate setup allows simultaneous measurement of ground state, pumped and reference signal
- Simultaneous measurement scheme, short monochromatic X-ray pulses, great time resolution and high repetition rate allow for previously unprecedent data quality

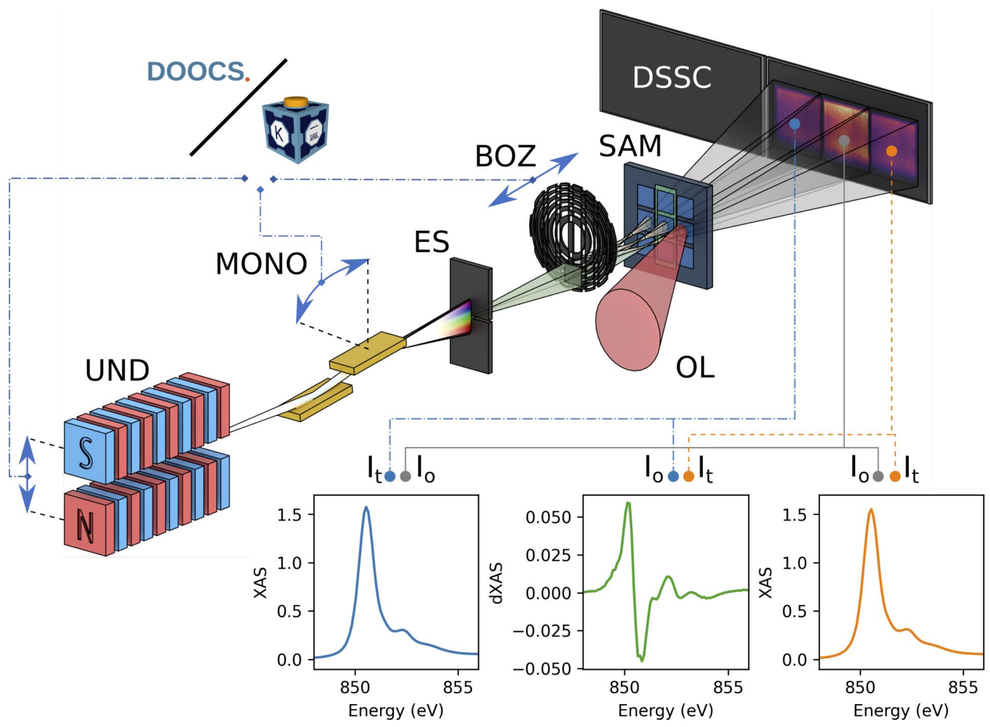

Figure 3: *Schematic depiction of the time-depend X-ray absorption spectroscopy measurement setup at the SCS instrument featuring the transmission zone plate with grating setup [4].*

Experimental Results

Experimental parameters:

- Pump: $h\nu$ = 4.66 eV, 35 fs duration and 0.8 (dn = 0.9%) and 4.0 mJ/cm^2 (dn = 4.7%) inc. fluence.
- Probe: **Ni**: $2p_{3/2}$ ($2p_{1/2}$) initial- → $3d$ final-states at the L_3 (L_2) edge **/ O**: $1s$ initial- → $2p$ final- states at the K edge.

Experimental results:

- At Δt = 0.5 ps (Fig. 3): ΔXAS has derivative-like shape (**Ni L_3 :**849 – 851.8 eV **/ O K**: 1st peak 528.5 – 532 eV)
  - ➢ Modelling (Fig. 4 (b)) shows spectral redshift and broadening
    - Not described: **Ni L_3 :** Pre-edge feature**/ O K:** Reduced intensity at 2nd and 3rd peak
- Transient ΔXAS (Fig. 4 (a)): builds up within the first 2 ps and is maintained over longer time
- From 0.5 ps ≤ Δt ≤ 10 ps (Fig. 4 (b)): Shape and intensity maintained
- Redshift and broadening increase slightly with dn (Fig. 4 (c)) → saturation region

GW plus embedded dynamical mean field theory (GW+EDMFT) calculations (Ni L_3):

- Energy shift from atomic cluster model:

$$\Delta E_{XAS} = [\Delta U_{dd} + \Delta\epsilon_d + \Delta\epsilon_c + \Delta U_{cd}] + [\Delta N_p(U_{pd} - U_{cp})]$$

  1. Screening of local coulomb interactions
  2. Nonlocal Coulomb interactions between photo-doped ligand holes and electrons (Hartree shifts)
- Calculated spectra from expended GW+EDMFT model show redshift (Fig. 6 (a,b))
  - ➢ Both effects contribute to the redshift with the strength depending on the contribution of the Hartree shifts (U_{cp}) (Fig. 6 (c))
  - ➢ Shift increases with photo-doping before saturation at 1% (Fig. 6 (c))

Two-band Hubbard model - multiplet calculations (Ni L_3):

- Multiplet description: Characterized by occupation of $3d$ band with initial state 2_h ($|\uparrow,\uparrow\rangle$): two unpaired electrons in two bands
- Equilibrium XAS: main weight in multiplet from transitions $2_h \rightarrow \underline{3}_d$ ($|\uparrow\downarrow,\uparrow\rangle$)
- Following photoexcitation: additional initial states available 2_l ($|\uparrow\downarrow,0\rangle$) , 2_s ($|\uparrow,\downarrow\rangle$) and 1_d ($|\uparrow,0\rangle$), allowing for additional transitions
- Transition $2_l \rightarrow \underline{3}_d$ matches pre-edge feature (Fig. 7 (a,b))

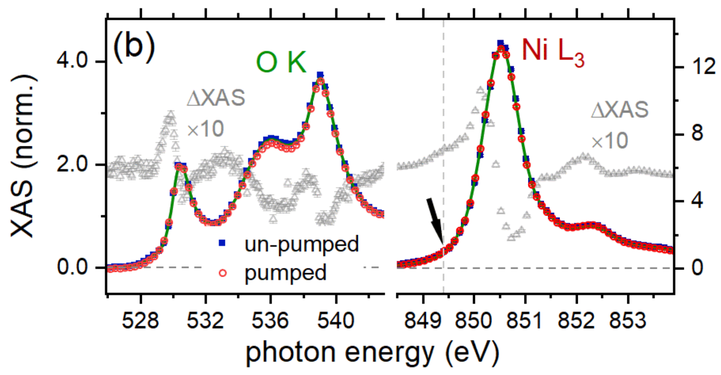

Figure 4: *(a) Un-pumped (□), pumped (•) and modelled (green line) absorption spectrum at Δt = 0.5 ps for the O K edge (left) and Ni L_3 edge (right), with Pump-induced change (■) overlayed [3] (modified)*

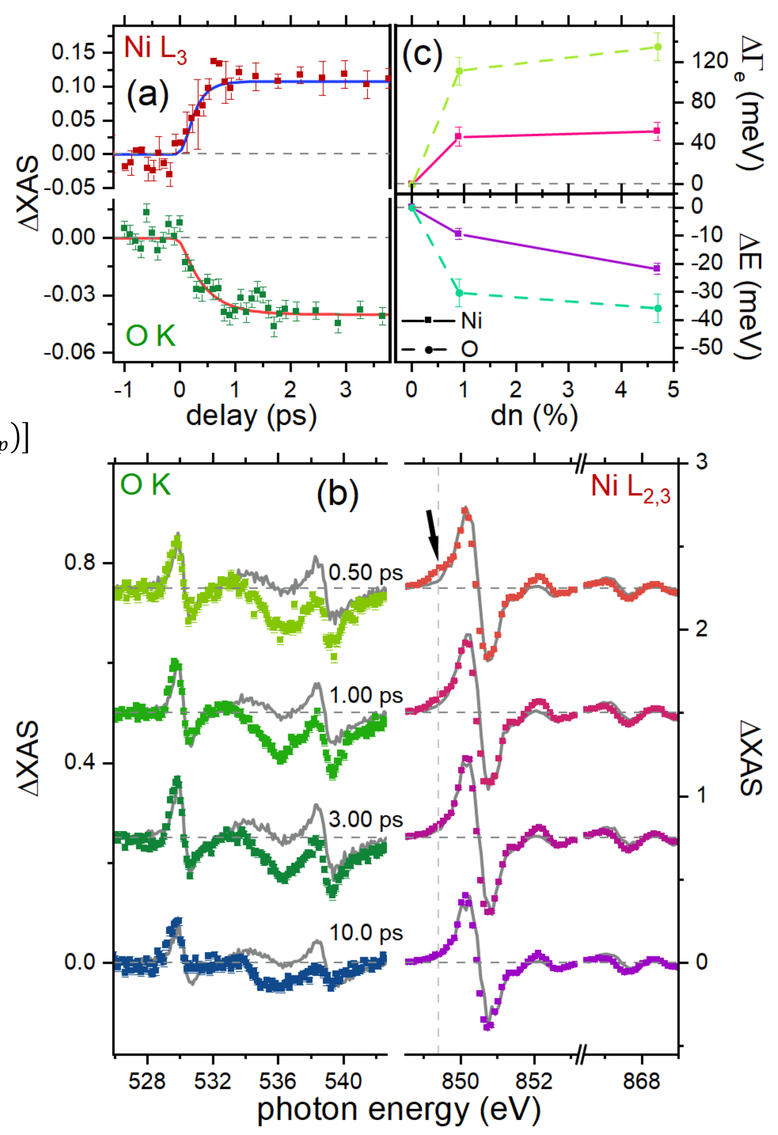

Figure 5: *(a) Time-dependent ΔXAS at Ni L_3 and O K edge with a fit (solid line). (b) Pump-induced changes ΔXAS at the indicated time delays from experiment (markers) with modelling for both edges and the corresponding values from modelling for both fluences (c)*

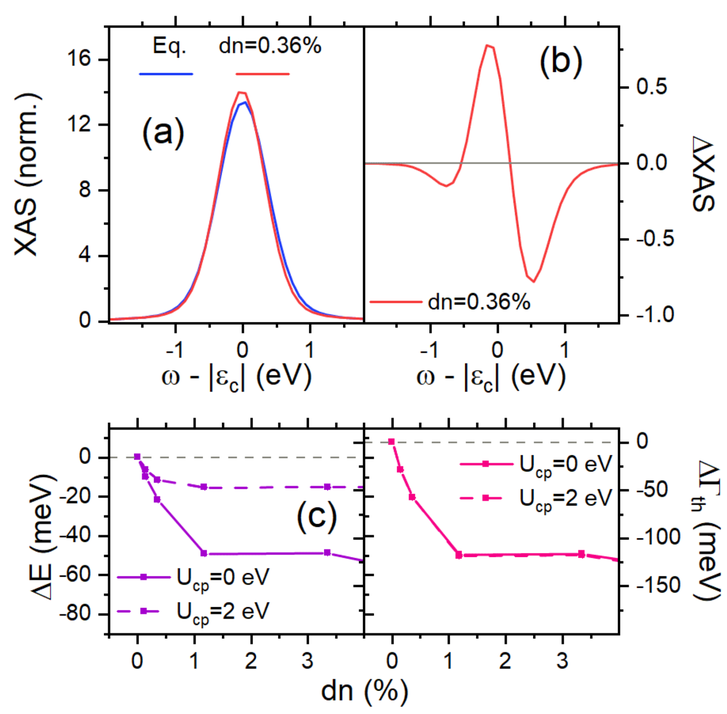

Figure 6: *(a) Pumped and unpumped absorption spectra calculated from GW+EDMFT with corresponding ΔXAS in panel (b). (c) Values of energy shift and narrowing for different photodoping*

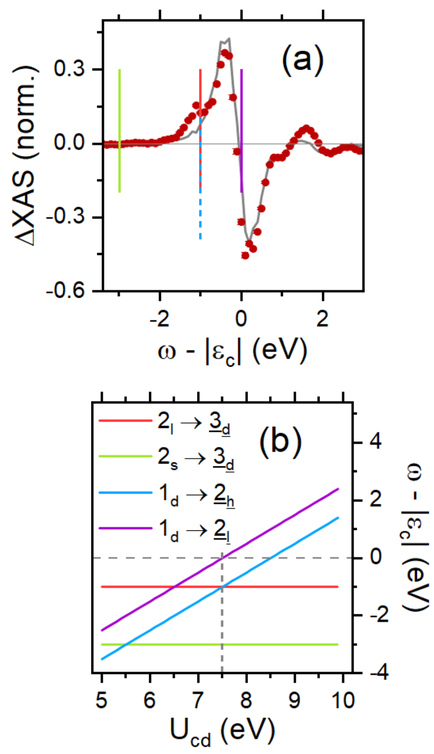

Figure 7: *(a) Un-pumped (□), pumped (•) and modelled (green line) absorption spectrum at Δt = 0.5 ps for the O K edge (left) and Ni L_3 edge (right), with Pump-induced change (■) overlayed [3] (modified)*

Conclusion

- Modelling of ΔXAS shows a spectral redshift as large contribution to induced changes at the **Ni $L_{2,3}$-edge**
- **Redshift dependents on electronic correlations as screening of local correlation and Hartree shifts depend on correlation effects of *d* and *p* electrons resp.**
- **Ni L_3 pre-edge feature indicates photoinduced Hund excitation with a larger contribution of the new initial state 2_l ($|\uparrow\downarrow,0\rangle$)**

Acknowledgements & References

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T. L. performed the experiments and analyzed the data. D. G. did the calculations. Both contributed equally to this work.

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