Investigating the interplay of local electron correlations and ultrafast spin dynamics in fcc Nickel at the European XFEL

T. Lojewski[1], M. F. Elhanoty[2], L. Le Guyader[3], O. Grånäs[2], N. Agarwal[3], C. Boeglin[4], R. Carley[3], A. Castoldi[5, 6], C. David[7], C. Deiter[3], F. Döring[7], R. Y. Engel[8], F. Erdinger[9], H. Fangohr[3, 10, 11], C. Fiorini[5, 6], P. Fischer[9], N. Gerasimova[3], R. Gort[3], F. de Groot[12], K. Hansen[8], S. Hauf[3], D. Hickin[3], M. Izquierdo[3], B. E. Van Kuiken[3], Y. Kvashnin[2], C.-H. Lambert[13], D. Lomidze[3], S. Maffessanti[8], L. Mercadier[3], G. Mercurio[3], P. S. Miedema[8], K. Ollefs[1], M. Pace[4], M. Porro[3, 14], J. Rezvani[15], B. Rösner[7], N. Rothenbach[1], A. Samartsev[3, 8], A. Scherz[3], J. Schlappa[3], C. Stamm[13, 16], M. Teichmann[3], P. Thunstrom[2], M. Turcato[3], A. Yaroslavtsev[2, 3], J. Zhu[3], M. Beye[8], H. Wende[1], U. Bovensiepen[1], O. Eriksson[2, 17], and A. Eschenlohr[1]

1. Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University Duisburg-Essen
2. Department of Physics and Astronomy, Uppsala University
3. European XFEL GmbH
4. Institut de Physique et Chimie des Matériaux de Strasbourg, University of Strasbourg, CNRS
5. Dipartimento di Elettronica, Informazione e Bioingegneria, Politecnico di Milano
6. Istituto Nazionale di Fisica Nucleare, Sez., Milano
7. Paul Scherrer Institut (PSI)
8. DESY Deutsches Elektronen-Synchrotron, DESY
9. Institute for Computer Engineering, University of Heidelberg
10. Max-Planck Institute for the Structure and Dynamics of Matter
11. University of Southampton
12. Materials Chemistry and Catalysis (MCC), Debye Institute for Nanomaterials Science, Utrecht University
13. Department of Materials, ETH Zurich
14. Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice
15. Laboratori Nazionali di Frascati, INFN
16. Institute for Electric Power Systems, University of Applied Sciences and Arts Northwestern Switzerland
17. School of Science and Technology, Orebro University

Motivation

Main Question: What influence do electronic correlations have during nonequilibrium dynamics in 3d transition metals?

Scientific background:

- Local correlations play a role in the emergence of magnetic order in 3d transition metals [1]
- **However:** Role of local correlations during nonequilibrium dynamics not yet been fully revealed (influence on electron dynamics, effects of possible screening)

Synopsis:

- Using femtosecond time-resolved X-ray absorption spectroscopy with time-dependent density functional theory we find that local Coulomb interactions influence the spin-dependent electron dynamics in fcc Nickel

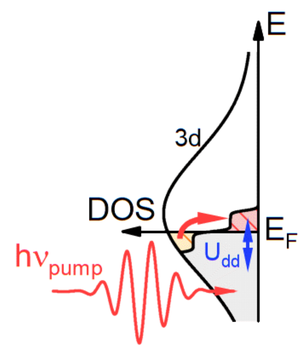

Figure 1: *Schematic representation of local correlations between hot (excited) electrons and other d-electrons*

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 electronic system
  - Probe after Δt (X-rays): Exciting core electrons into unoccupied electronic states

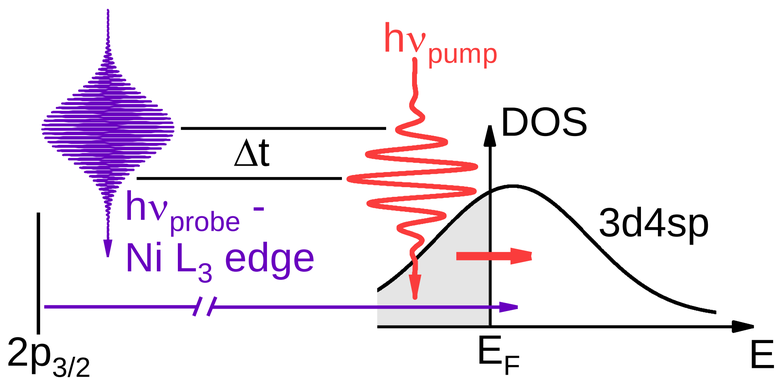

Figure 2: *Sketch of the time-resolved optical pump, x-ray absorption probe experiment at the Ni L_3 absorption edge (2p3/2 → 3d) with time delay Δt. [3] (modified).*

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

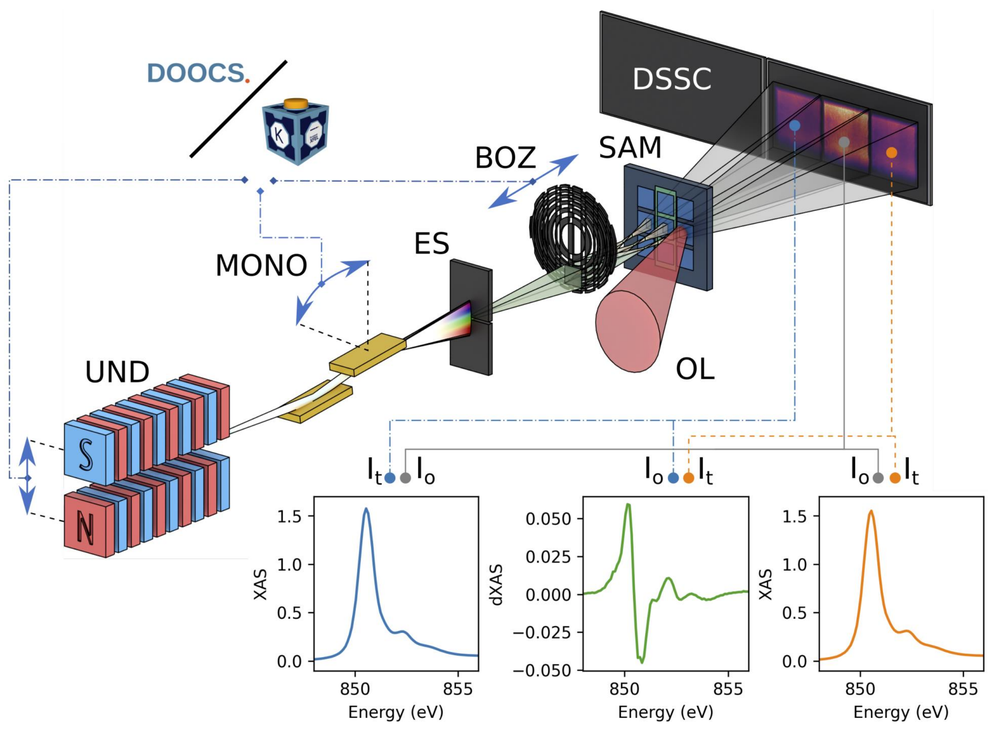

Figure 3: *Schematic depiction of the time-depend X-ray absorption spectroscopy measurement setup at the SCS instrument featuring the transmission zone plate with grating setup [4].*

Acknowledgements & References

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T. L. performed the experiments and analyzed the data. M. E. developed the extension of TDDFT and did the calculations. Both contributed equally to this work.

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Contact: tobias.lojewski@uni-due.de

Experimental & Theoretical Results

Experimental parameters:

- Pump: $h\nu$ = 1.5 eV, 35 fs duration and 12 mJ/cm^2 inc. fluence
- Probe: Transition from $2p_{3/2}$ ($2p_{1/2}$) initial- → $3d$ final- states at the L_3 (L_2) edge

Experimental results:

- At Δt = 0.4 ps (Fig. 4 (a/b)): ΔXAS has derivative-like shape (852 - 852.8 eV positive / 853 – 854 eV negative)
  - ➢ Modelling shows spectral redshift (104 ± 25 meV) and broadening (139 ± 10 meV)
- From 0.4 ps ≤ Δt ≤ 3.5 ps (Fig. 6 (a)): Induced change is reduced, shape is maintained
- L_2 edge: ΔXAS energetically broader, resulting from larger lifetime broadening (Fig. 6 (a)) [8]
- Transient ΔXAS: fast initial excitation (within 200 fs) and subsequent decay over 1 ps

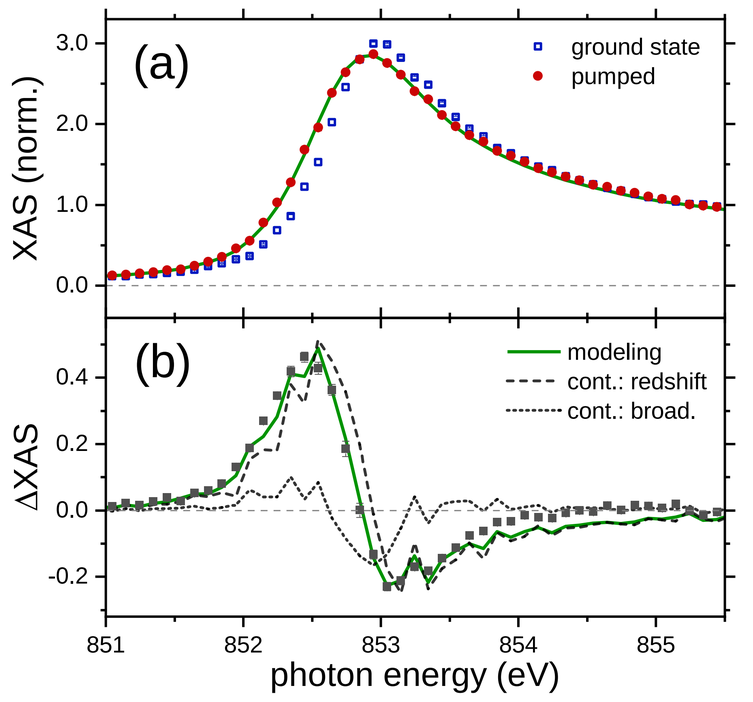

Figure 4: *(a) Ground state (□), pumped (•) and modelled (green line) absorption spectrum at Δt = 0.4 ps. (b) Pump-induced change (■), the modelled result (green line) and the contribution of the shift (dashed)/broadening (dotted) [3] (modified).*

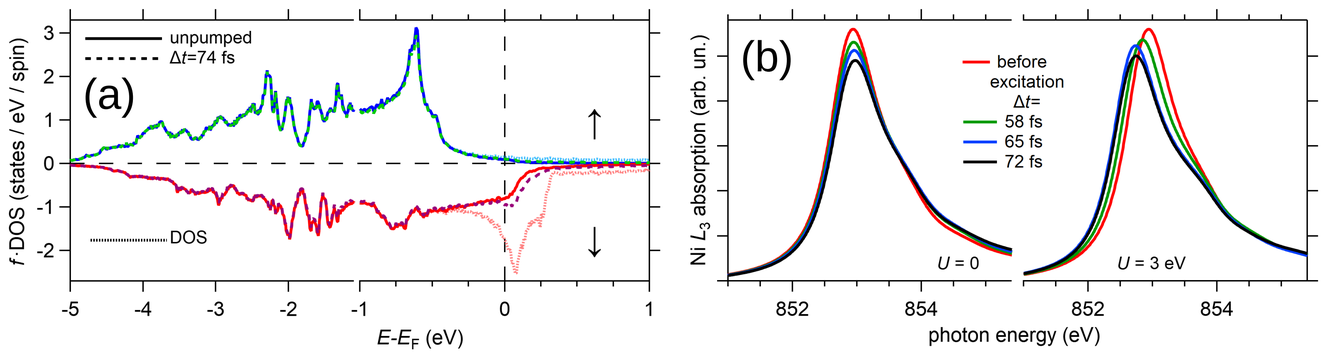

Figure 5: *(a) Populated exchange-split DOS in fcc Ni calculated by TDDFT for majority (↑) and minority (↓) states before optical excitation (solid lines) and at Δt = 74 fs (dashed lines). Static DOS without population is shown for comparison (dotted lines). (b) Absorption spectrum of the Ni L3 edge after optical excitation calculated by TDDFT using the transient f · DOS from panel (a) (left) and also including U = 3 eV (right). [3] (modified)*

Time-dependent density functional theory:

- Calculating occupied DOS as $f(E,t)\cdot\mathrm{DOS}(E,t)$ (Fig. 5 (a)):
  - For Δt ≤ 74 fs: Increased occupation in $3d_\downarrow$ (minority) channel, decreased occupation in $3d_\uparrow$ (majority) channel
  - ➢ Induced spin currents → spin-flip transitions → reduced m
- Calculating tr-XAS in general approach using:

$$\chi_0(\omega) = \lim_{\eta\to 0}\sum_{ijk}(f_{ik}-f_{jk})\frac{\phi^*_{ik}(r)\phi^*_{jk}(r')\phi_{ik}(r')\phi_{jk}(r)}{\omega-(\epsilon_i-\epsilon_j)+i\eta}$$

  - ➢ Reproduces only broadening (Fig 5 (b))
- Introducing electronic correlations U using a single-band Hubbard model:

$$\chi_0^H(\omega) = \lim_{\eta\to 0}\sum_{ijk}(f_{ik}-f_{jk})\frac{\phi^*_{ik}(r)\phi^*_{jk}(r')\phi_{ik}(r')\phi_{jk}(r)}{\omega-(\epsilon_i-\epsilon_j+U\cdot m)+i\eta}$$

  - ➢ **Excitations of initial ground states $(\epsilon_i-\epsilon_j)$ which experiences spin flips have a shifted excitation energy by $\mathbf{U\cdot m}$**
- Comparison with Experiment (Δt = 0.4 ps) (Fig. 6 (a)):
  - For U = 0 Qualitative difference in shape, for U = 3 good agreement

➢ **Inclusion of local correlations necessary to describe emergence of energy shift on ultrafast timescales**

Density functional theory:

- For Δt ≥ 0.5 ps: Reproducing ΔXAS by calculation with elevated electronic temperature T_e and reduced magnetic moment μ
  - Relaxation of elevated T_e and reduced μ reproduces ΔXAS between 0.5 ps ≤ Δt ≤ 3.5 ps (Fig. 6 (a,b))

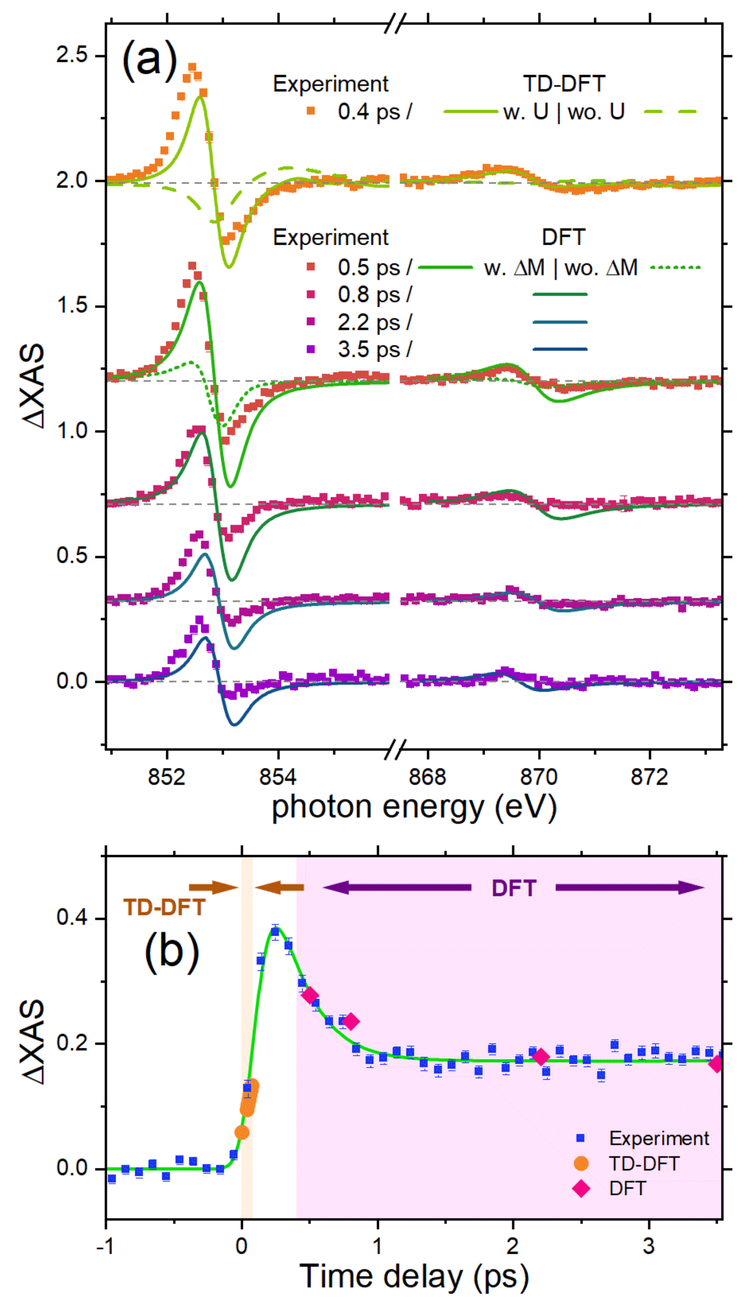

Figure 6: *(a) ΔXAS at the indicated time delays from experiment (markers) and TDDFT/DFT calculations (lines). (b) Time-dependent ΔXAS at hv = 852.72 eV with a fit (green line) and the corresponding values from TDDFT (convoluted with a Gaussian of 80 fs FWHM) and DFT, as indicated. [3]*

Summary & Conclusion

- Modelling of ΔXAS with Spectral redshift (104 ± 25 meV) and broadening (139 ± 10 meV)
- Successful description with novel TDDFT calculations including electronic correlations

- **The spectral redshift is a result of the influence of local electronic correlations on the spin-dependent electron dynamics in Nickel**