Femtosecond time-resolved and element-specific x-ray absorption spectroscopy of Fe/MgO

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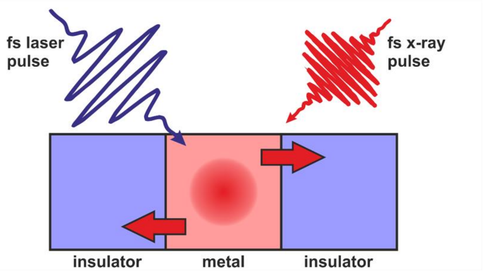
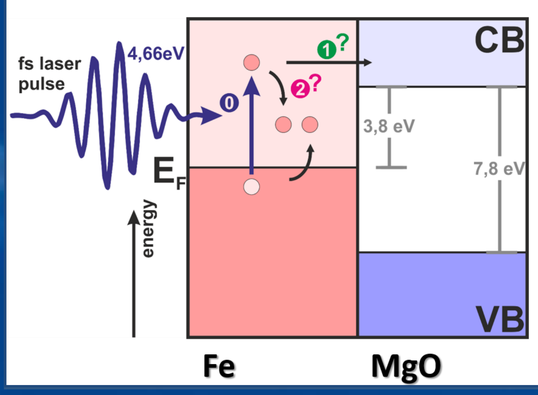
Introduction



Local excitation of a heterostructure:

- Energy flow between different constituents?

→ Investigating a metal/insulator heterostructure can provide direct insight into microscopic, dynamic redistribution of excitation



Possible ultrafast dynamics?

0 fs UV-laser excites locally the electronic system

1 Direct charge transfer across the interface?

2 Excitation stays localized in Fe and couples to low energy excitations?

Figure: Top: Schematic representation of the energy flow between different constituents after localized excitation of a heterostructure. Bottom: Schematic representation of the electronic structure of an Fe/MgO interface. [1] The possible ultrafast processes in the metal/insulator heterostructure after localized optical excitation are indicated.

Experimental method: time-resolved XAS

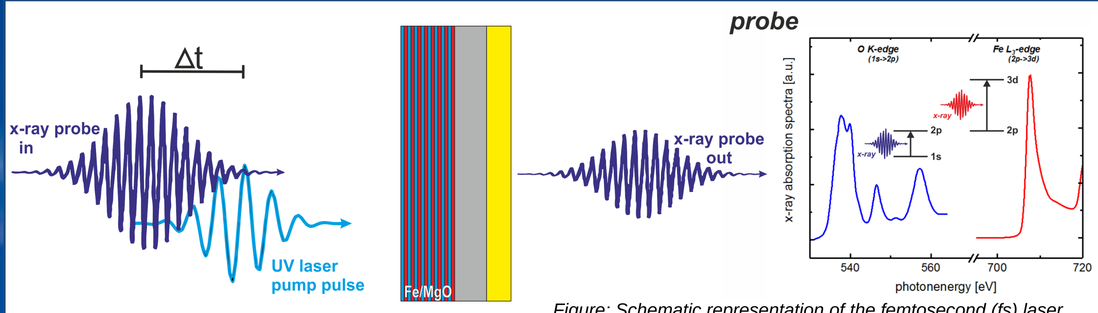


Figure: Schematic representation of the femtosecond (fs) laser pump x-ray probe experiment in transmission geometry. Illustration of x-ray absorption at the O K-edge and Fe L-edge.

Fs laser pump fs x-ray probe experiment:

→ Identify electronic and lattice excitations by their characteristic timescales

→ Element-specific probe allows being selective for single constituents

- Settings:
  - → 70 fs laser pump (λ_L = 266 nm) and 100 fs x-ray probe pulses
  - → 150 fs total time resolution

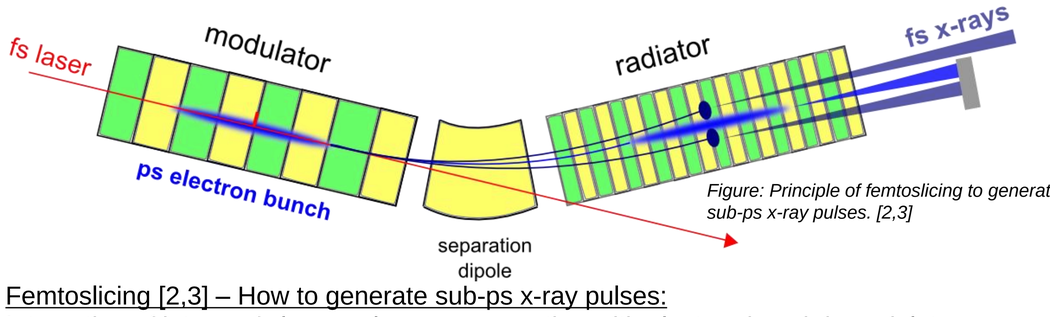


Figure: Principle of femtoslicing to generate sub-ps x-ray pulses. [2,3]

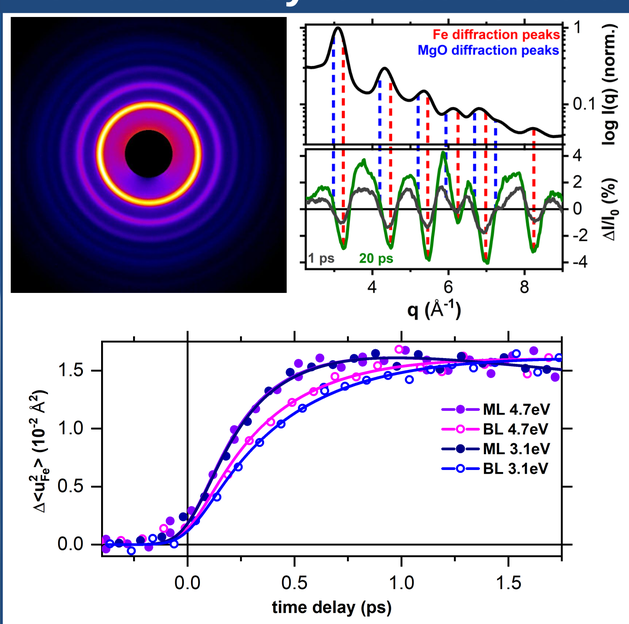
Femtoslicing [2,3] – How to generate sub-ps x-ray pulses:
Interaction of intense fs laser pulse co-propagating with electron bunch in undulator

→ Electric field of laser modulates energy of part of electrons in bunch

→ „Sliced“ electrons take different path in subsequent dipole magnet

→ Femtosecond x-ray pulses are spatially separated

Structural dynamics: Ultrafast electron diffraction



Result ultrafast electron diffraction:

- Diffraction peaks of Fe and MgO overlap in most cases because of experimental resolution (0.14 Å^{-1})

→ Only Fe-response can be isolated

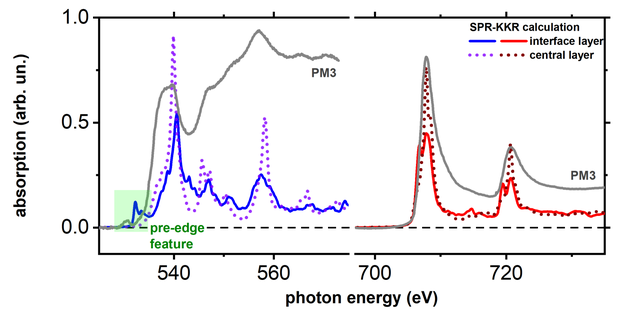
- Excitation of lattice occurs within few hundred fs
- Excitation independent of pump photon energy
- Excitation exhibits clear differences for different sample structures

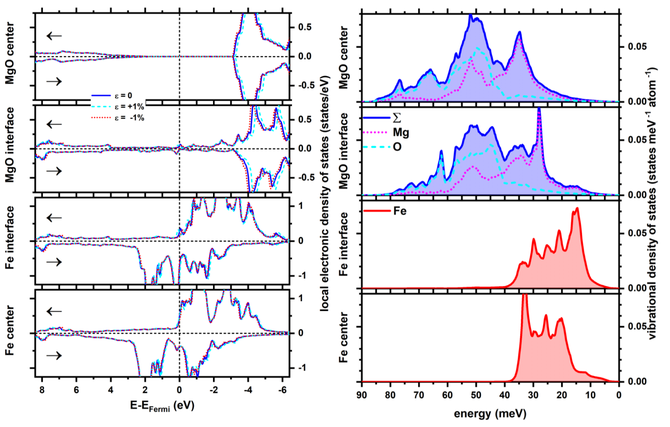
→ Interface mediated coupling speeds up electron-lattice equilibration in Fe

→ Phononic processes at interface are essential

Figure: Top left: Diffraction image of [2nm Fe/5nm MgO]$_5$ without laser pumping. Top right: Diffraction signal by azimuthal integration along lines of constant momentum transfer and diffraction intensity changes for time delays of 1 ps and 20 ps after excitation with 4.7 eV laser pulse. The red- and blue-dashed lines mark positions of diffraction peaks of Fe and MgO, respectively. Bottom: Change of the r.m.s. displacement as function of time delay for different sample configurations (ML: [2 nm Fe/5 nm MgO]$_5$ and BL: [10 nm Fe/ 25 nm MgO]$_1$) and excitation conditions. Experiments were carried out at SLAC National Accelerator Laboratory [4] using electron pulses with 200 fs FWHM and kinetic energy of 3.7 meV. The pump-fluence was 9 mJ/cm².

ab initio DFT calculations





High resolution XAS:

- Static x-ray absorption spectra show detailed fine structure
- For Fe interface induced changes are not resolved in experiment

→ SPR-KKR calculations reveal measured O K pre-edge feature results from interface states

Figure: Comparison of experimental high resolution x-ray absorption spectra (grey “PM3” curve) with layer-resolved first principle calculations for the oxygen K-edge and iron L-edge. The O K pre-edge feature is highlighted.

Local electronic density of states:

- Interface states due to hybridization of Fe and O orbitals
- Hybridized states are very sensitive to local lattice distortions

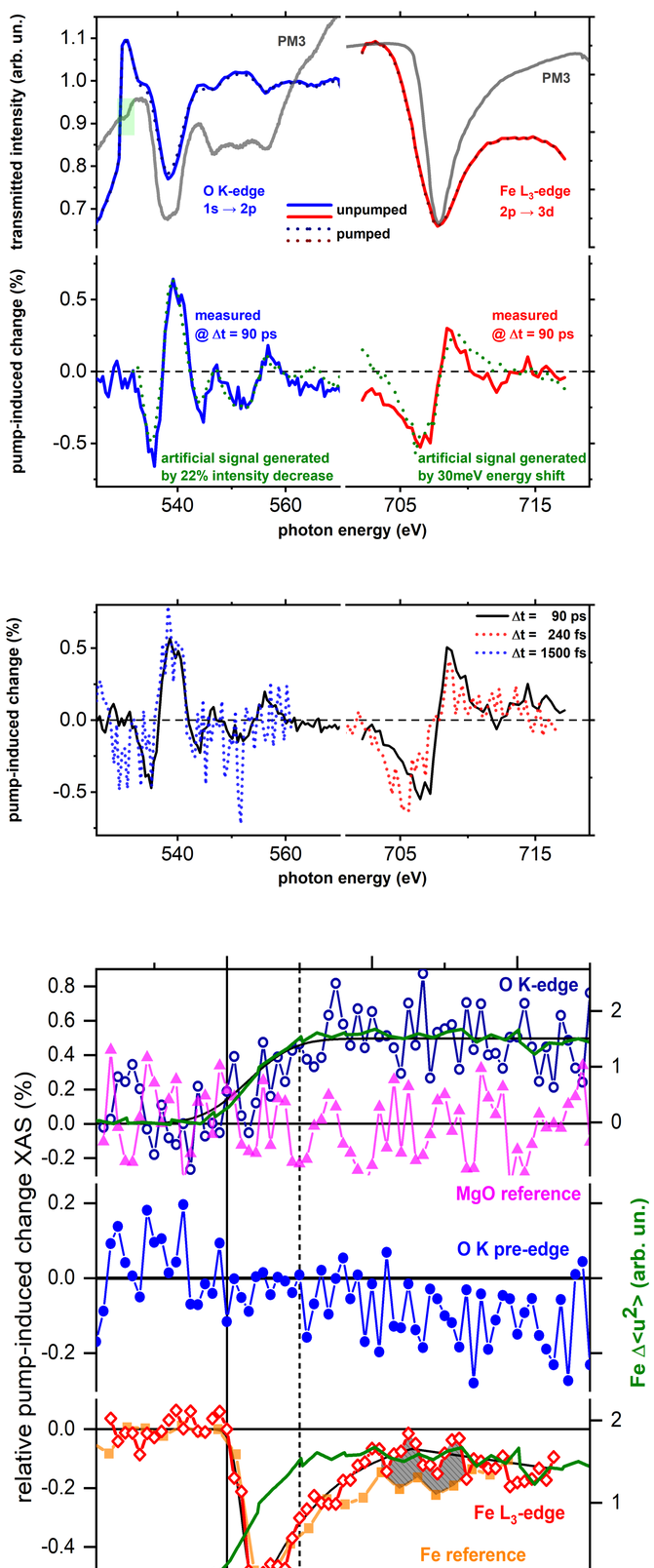
Local vibrational density of states:

- MgO VDOS above acoustic phonons
- Sizable Fe VDOS at these high energies

→ Phononic transfer of excitation across interface mediated at phonon energies above 15 meV

Figure: Left: Layer-resolved electronic density of states under 1% compression and expansion of Fe$_8$/(MgO)$_8$(001) at the Fe-MgO interface obtained from DFT calculations. Right: Layer-resolved vibrational density of states of Fe$_8$/(MgO)$_8$(001) obtained from DFT calculations.

Femtosecond time-resolved XAS



How to understand the pump-induced effect?

- Energy shift of absorption edge upon laser excitation known for metal systems [5,6]

→ Fe L_3-edge: Pump-induced excitation lead to a shift of unpumped spectra by 30 meV

→ O K-edge: Pump-induced excitation lead to an intensity decrease of unpumped spectra by 22 %

Figure: Top: Transmitted soft x-ray intensity as a function of photon energy measured at the FemtoSpeX beamline for the oxygen K-edge (left side) and Fe L_3-edge (right side) with 50 picosecond time resolution with and without laser pumping. Comparison to transmitted soft x-ray intensity measured with higher energy resolution (grey “PM3” curves, see Figure above). Bottom: Relative pump-induced change as a function of x-ray photon energy at a pump-probe delay of 90ps. The green-dashed curves depict artificial signals generated out of simple modeling from the measured unpumped spectra. The pump-fluence was 20 mJ/cm².

Spectral changes ps vs. fs:

- Pump-induced change with fs time resolution has similar shape as change with ps time resolution

Figure: Relative pump-induced change as a function of x-ray photon energy for the oxygen K-edge (left side) and Fe L_3-edge (right side) with 150 femtosecond time resolution at pump-probe delay of the maximum observed change at the indicated time delays. Comparison with the pump-induced change with 50 picosecond time resolution. The pump-fluence was 20 mJ/cm².

Results of femtosecond delay scans:

After 500 fs:

- Fe went through extremum & relaxes
- O K-edge just reached maximum
- O K pre-edge is still building up
- Fe reference sample shows additional phononic relaxation channel via Fe/MgO interface

→ Different behavior of Fe & O transients

→ Energy transfer between Fe and MgO not purely electronic

Dynamics on < 1 ps timescale:

- Fe phonons initially excited by Fe electrons
- (subset) MgO phonons initially excited by Fe

→ Non-thermal phonon population important for coupling across interface

Dynamics on > 1 ps timescale:

- Fe UED-signal shows further relaxation to MgO ph
- Interface-mediated dynamics also on > 1 ps
- On > 1 ps timescale a local lattice distortion at interface builds up

Figure: Pump-induced changes at three selected photon energies in combination with the change of the Fe r.m.s. displacement as a function of pump-probe delays for Fe/MgO multilayer sample compared with the pump-induced changes for a pure Fe and MgO reference sample. First panel: O K-edge and changes in the Fe r.m.s. displacement. Second panel: O K pre-edge. Third panel: Fe L_3-edge and changes in the Fe r.m.s. displacement same as in first panel. The black curves are fitted by analytical functions. The pump-fluence was 20 mJ/cm² and 9 mJ/cm² for tr-XAS and tr-electron diffraction, respectively.

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Conclusion

- After pumping one constituent in a metal/insulator heterostructure with a UV laser pulse, we see by element-specific probe a clear pump effect at both edges in ps and fs time resolution
- Microscopic access to energy flow dynamics in Fe/MgO heterostructures by combining fs time-resolved, element-sensitive XAS and ultrafast electron diffraction, complemented by ab initio theory
- The measured spectra can be described by generating an artificial pumped signal by shifting the unpumped spectra to smaller energies (Fe edge) or decreasing the intensity of the absorption fine structure (O edge)
- Interface-mediated relaxation channel for phonons in Fe to MgO
- Coupling to MgO on two different timescales emphasizes importance of non-thermal phonon populations