Femtosecond Near Edge X-ray Absorption Measurement of the VO_2 Phase Transition.

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Abstract: We measure the insulator-to-metal transition in VO_2 using femtosecond Near-Edge X-ray Absorption. Sliced pulses of synchrotron radiation are used to detect the photo-induced dynamics at the 516-eV Vanadium L_3 edge.
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Time-resolved spectroscopy can probe new physical pathways of phase transitions and reveal fundamental aspects that are hidden in time-integrated measurements. However, limited quantitative information about electronic structure can be extracted from measurements at visible wavelengths, motivating interest in short-pulse x-ray spectroscopy.

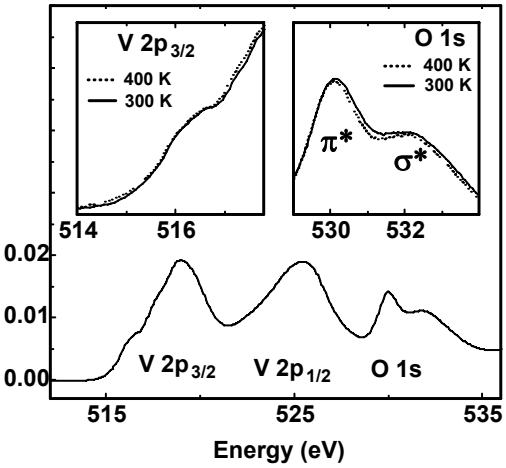

Figure 1. Static, VO_2 x-ray absorption spectra in the region around the V $L_{2,3}$ and the O K edge. Spectral changes at the V Ledge and the O K edge observed above 340 K

Near-edge X-ray absorption spectroscopy techniques probe unoccupied valence states by measuring transitions from core levels, rather than from extended occupied valence states as in visible spectroscopy. Element specificity, symmetry selection rules and linear/circular dichroic effects are some of its most powerful aspects. Due to the stringent tunability requirements on the source, time-resolved spectroscopy with soft x-rays is ideally performed using synchrotron radiation. Novel laser e-electron beam interaction schemes provide schemes to access the sub-picosecond time domain. Here, we report on picosecond and femtosecond soft x-ray absorption measurements of the insulator-to-metal transition in photo-

excited VO_2. a non-magnetic compound that undergoes a transition between a monoclinic insulator and a rutile metal when heated above 340 K. Previous ultrafast optical and x-ray diffraction experiments [3] on the photo-induced transition in VO_2 show that changes in both atomic and electronic structure occur on the sub-picosecond timescale, where their detailed relationship is yet to be fully understood. The experiments discussed here are performed either with the full 70-ps pulse of the Advanced Light Source [1] or exploiting laser modulation of electron bunches [2].

Picosecond XAS measurements: Time-resolved XAS experiments were performed using bend magnet radiation at beamline 5.3.1 of the Advanced Light Source. 70-ps x-ray pulses were radiated by a bend magnet and focused onto the VO_2 sample using a toroidally bent silicon mirror, which imaged the e-beam into the x-ray hutch. A fraction of the x-ray pulses, radiated once every 656 ns (roundtrip time of the storage ring), were used for our experiments at 1-KHz repetition rate. A flat-field imaging spectrometer was used to disperse the transmitted soft x-rays after the sample, generating spectra in the range between 100 eV and 800 eV, with a resolution of approximately 4 eV at 500 eV.

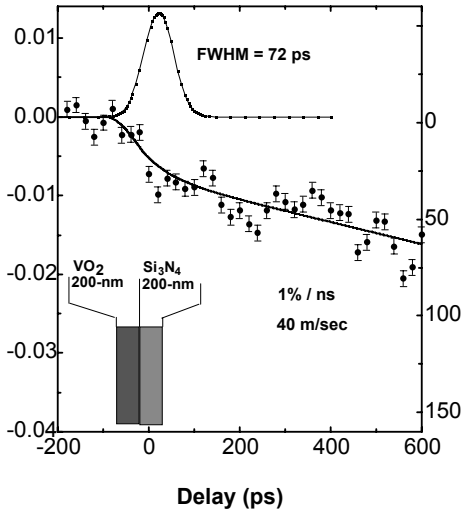

Figure 2: Time-resolved transmission changes at the Vanadium L_3 edge.

Differential transmission measurements at the Vanadium L_3 edge show the expected decrease in the transmission of the sample, due to the photo-induced collapse of the bandgap. The data in figure 2 are fit with a fast response corresponding to $\Delta T/T \approx 1\%$, followed by a slower decrease at a rate of approximately 1%/ns. Since the thickness of the transformed layer scales linearly with the signal, we estimate that a fast transformation over approximately the first 50-nm occurs within the x-ray probe pulse, followed by slower thermal growth at 40 m/sec.

Femtosecond XAS measurements: Femtosecond XAS was performed using the same apparatus described above, combined with laser modulation of electron bunches in the wiggler of straight section 5 of the storage ring. A pair of slits was placed in the x-ray hutch at the image plane of the storage ring, immediately before the VO_2 windows, effectively isolating the image of the femtosecond x-ray source in the spatial wings of the beam. The flux in the femtosecond x-rays was approximately four orders of magnitude lower than in the picosecond pulse, amounting to a few thousand photons/(sec 1% BW) at 500 eV in a 1-KHz train. Sample transmission (30%), spectrometer efficiency (6%) and detector efficiency (50%) resulted in about 10 photons/sec in the 0.5% bandwidth where the experiment was performed.

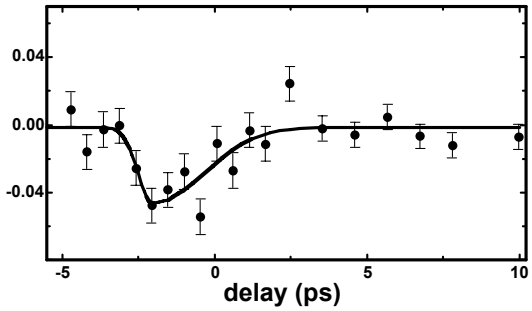

Figure 3: Femtosecond dynamics of the as measured at the V L_3 edge. The experiments probe unoccupied d states after excitation, resulting in increased absorption.

The femtosecond, time-resolved response is reported in figure 3, where a prompt drop in the transmission of the sample can be observed immediately after laser excitation. This drop is interpreted as the effect of holes created in the valence bands of d symmetry, while electrons are promoted to the conduction band, formed by orbitals of mixed p-d character and therefore less evident at the V L edges. Thus Ledge measurements are more sensitive to the holes of purely d symmetry (causing over absorption) than to the electrons in the conduction band. Future measurements will probe also the conduction band at the Oxygen 1s edge.

In summary, we report the first soft X-ray absorption measurement with femtosecond resolution, demonstrated for the photo-induced insulator-to-metal transition in the strongly correlated compound VO_2. In the picosecond measurements we detect a shift of the Vanadium L_3 edge, associated with the collapse of the bandgap. We also report on the first femtosecond soft XAS measurement, which reveal the early photo-doping process through a drop in transmission at the VL_3 edge.

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[2] R.W. Schoenlein et al. *Science* **287**, 2237 (2000)

[3] A. Cavalleri et al. *Phys. Rev. Lett.* **87**, 237401 (2001).