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Time-resolved near-edge x-ray absorption fine structure spectroscopy on photo-induced phase transitions using a tabletop soft-x-ray spectrometer

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We present a table-top soft-x-ray spectrometer for the wavelength range $\lambda = 1$–5 nm based on a stable laser-driven x-ray source, making use of a gas-puff target. With this setup, optical light-pump/soft-x-ray probe near-edge x-ray absorption fine structure (NEXAFS) experiments with a temporal resolution of about 230 ps are feasible. Pump-probe NEXAFS measurements were carried out in the "water-window" region (2.28 nm–4.36 nm) on the manganite $Pr_{0.7}Ca_{0.3}MnO_3$, investigating diminutive changes of the oxygen K edge that derive from an optically induced phase transition. The results show the practicability of the table-top soft-x-ray spectrometer on demanding investigations so far exclusively conducted at synchrotron radiation sources. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4718936]

I. INTRODUCTION

While the development of sources for future lithography at 13.5 nm advances rapidly,[1,2] also applications beyond lithography are devised and improved in the EUV/soft-x-ray region (100 nm–1 nm). The development of laboratory-sized table-top soft-x-ray sources has led to an ever growing interest in setups for x-ray microscopy in the EUV and "water-window" region (2.28 nm–4.36 nm; Refs. 3–5) and absorption spectroscopy at the K edges of low Z elements.[6–9] Too, the use of an optically pump/soft-x-ray probe setup of table-top size has been demonstrated for nanosecond time-resolved x-ray diffraction experiments.[10–12]

Time-resolved absorption spectroscopy, a powerful tool for investigations of the near-edge x-ray absorption fine structure (NEXAFS) for elemental and chemical analysis on the other hand, is so far almost exclusively performed at synchrotrons. Time-resolved NEXAFS spectroscopy can be used to obtain element specific information, as it probes intermolecular bonds and distances, giving rise to changes in oxidation states and the temporal evolution of these changes. Amongst others, it can be used to study transient changes in the electronic structures due to photo-induced phase transitions in elements and alloys, such as the insulator-to-metal transition in manganites such as $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO).[13] Phase transitions of various kinds of this and other colossal magnetoresistive (CMR) manganites have been of great interest as to understand the underlying mechanisms leading to these interesting material behaviors.[14–16]

Here, we demonstrate the feasibility of conducting time-resolved NEXAFS measurements on the optically induced melting of the charge-ordered phase in PCMO with the aforementioned table-top size soft-x-ray setup. The measurements on the transient changes due to the electronic structure of the photo-induced phase transition were carried out with a temporal resolution of about 230 ps and the change in absorption on the oxygen K edge due to this phase transition was determined.

II. SETUP AND EXPERIMENTS

The time-resolved NEXAFS experiments were performed in a vacuum system (Fig. 1), as the mean free path of soft-x-ray radiation in air is less than 1 mm. The x-ray source is based on a laser-induced plasma, making use of a ps laser system (Ekspla, SL312P, $\lambda = 1064$ nm, f = 5 Hz, $t_{pulse} = 170$ ps) and a gas-puff target. Krypton is used as a target gas, as its emission spectrum is very strong and continuous in the spectral region of the water-window due to a large number of emission lines from transitions in K-like (XVIII) to H-like (XXXVI) krypton ions,[17,18] making it an ideal emitter for spectroscopic investigations.[9] The laser beam is focused into the source chamber and synchronized with a short gas pulse created by a piezo-driven fast gas valve (Proch-Trickl type,[19] backing pressure 10 bar). The duration of the gas pulse of ~900 μs stems from the compromise between a high target density and a gas load that is as small as possible. The light emitted from the hot and dense krypton plasma is filtered by an aluminum filter (thickness 200 nm), eliminating out-of-band radiation, such as visible light.

The soft-x-ray spectrometer consists of an entrance slit (d = 100 μm), an aberration-corrected concave grating (Hitachi, 2400 grooves/mm, wavelength range 1–5 nm) and a backside-illuminated CCD camera (Roper Scientific, 2048 × 512 pixels, 13 μm × 13 μm pixel size). With this setup the complete spectrum of the soft-x-ray plasma between 300 eV and 1050 eV is recorded at once within a single laser pulse. The energy resolution was estimated with the nitrogen

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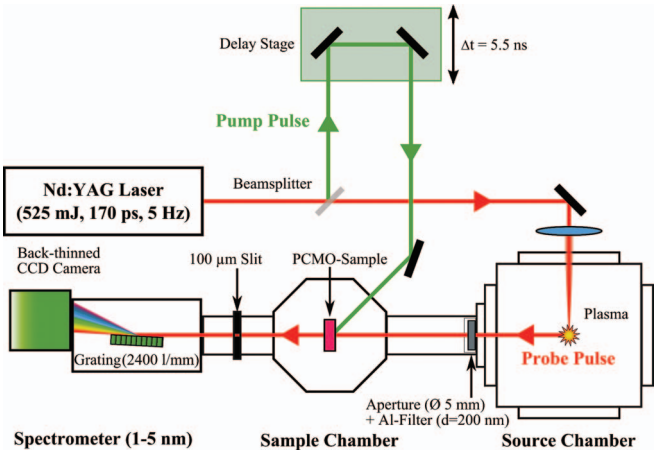

FIG. 1. Experimental setup used for the pump-probe NEXAFS spectroscopy measurements. The sample chamber is equipped with a cryostat cooling system based on liquid nitrogen.

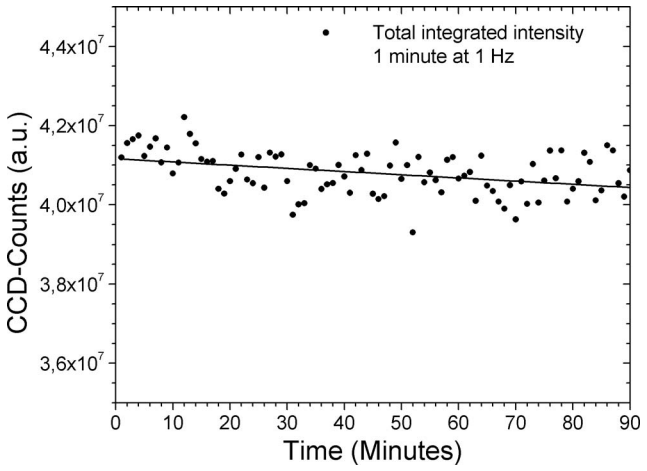

FIG. 2. Long term stability of the plasma intensity (f = 1 Hz). Each data point represents the total integrated intensity of 60 krypton spectra (i.e., 1 min).

emission line at E = 430.695 eV ($1s^2$-$1s2p$, *NVI*). A fitting procedure using a Gaussian curve results in a linewidth of ΔE = 1.08 eV and therefore an energy resolution of E/ΔE ≈ 400.

Using a beam splitter, 4% of the ps laser pulse used to generate the soft-x-ray probe beam is directed to a variable delay stage, providing a NIR pump beam. The laser pulse energy was set to 240 mJ, leading to a pump pulse of ∼9 mJ. The temporal overlap between the two pulses at the sample position was determined with an ultrafast photodiode, a fast oscilloscope (Tektronix, DPO 7254, 2.5 GHz, 40 GS/s) and the known path differences in the beam paths. The delay stage allowed for a delay of −2.0 ns to +3.5 ns between the pump pulse and the probe pulse at the sample surface. The pump beam diameter was focused from 16 mm to 5 mm onto the sample surface, resulting in a fluence of ∼30 mJ/cm^2, sufficient to induce a transient metallic phase in PCMO (Ref. 20) optically.

In the sample chamber, the PCMO sample is cooled down to 100 K with liquid nitrogen by a cryostat (Oxford Instruments, Mikrostat, temperature stability +/−0.1 K). The sample was fixed on the cryostat via a copper frame, ensuring a uniform temperature over the sample size. The sample temperature was set to 100 K in order to establish the charge-ordered phase in the PCMO and the sample surface was positioned perpendicular to the probe-beam propagation. The pump pulse was directed at an angle of incidence of 45° to the center of the sample.

Optically pump/soft-x-ray probe spectroscopy has been performed on a thin layer (200 nm) of PCMO, deposited onto a Si_3N_4 sample window via pulsed laser deposition at room temperature at the Institut für Materialphysik, University of Göttingen. After deposition, the PCMO thin layer was annealed for 15 h at 700 °C under air and the crystal structure was verified via x-ray diffraction (space group Pbnm).

The PCMO thin film was investigated via x-ray photoelectron spectroscopy, the Mn^{4+}/Mn^{3+} ratio was verified to comply with the doping level and appropriate literature values (IPPT, Technical University, Clausthal).[21–23] The measurements were performed at room temperature in an ultra-high vacuum apparatus with a base pressure of 5 × 10^{-11} hPa (Ref. 24) using a hemispherical analyzer (VSW HA100) and a commercial non-monochromatic x-ray source (Specs RQ20/38C). For the measurement, the Al K_α line (photon energy 1486.7 eV) was used.

In order to measure the diminutive changes in the oxygen K edge resulting from the photo-induced phase transition, a high reproducibility over the course of the measurement (1 h and more) had to be maintained. This was achieved by using the laser with a repetition frequency of 1 Hz, as the laser pulse energy and consequently the intensity of the soft-x-ray plasma gets instable at higher repetition rates. Figure 2 shows the stability of the plasma intensity vs. time. Over the course of 90 min (5400 pulses), the intensity drops by 0.78% while showing a standard deviation in relation to the mean value of only 1.3%.

In comparison to measurements at synchrotron radiation sources, where NEXAFS spectra are determined through the fluorescence yield or Auger electrons originating from the irradiated sample, transmission measurements are carried out with the table-top setup. For transmission measurements, NEXAFS spectra are obtained by calculating he optical thickness *OD* according to Lambert-Beer's law

$$OD_{Sample} = -ln\left(\frac{I_S}{I_0}\right), \tag{1}$$

where I_S represents the transmitted (i.e., sample) and I_0 the reference intensity.

Phase transitions leading to changes in, e.g., bond lengths or oxidation states will result in altered intensities of absorption edges and can be described by

$$OD_E - OD_R = -ln\left(\frac{I_E}{I_0}\right) + ln\left(\frac{I_R}{I_0}\right) = -ln\left(\frac{I_E}{I_R}\right) \tag{2}$$

with OD_E and I_E being from the excited and OD_R and I_R being from the reference sample measurement, respectively. As can be seen, the change in absorption due to a phase transition can be determined with transmission spectra alone. This way, no moving of the sample was needed as both spectra could be measured after passing through the sample, facilitating the

measurement procedure. Furthermore, the transmission at the same position of the sample was achieved.

To further enhance the sensitivity during the measurement, for each delay time the spectra were accumulated over 100 pulses, and for each sample measurement one reference measurement was performed. The reference spectra were recorded with a time delay of $\Delta t = -2.0$ ns and therefore well before the excitation of the sample through the pump pulse.

III. RESULTS AND DISCUSSION

A static NEXAFS spectrum of $Pr_{0.7}Ca_{0.3}MnO_3$ is shown in Fig. 3, exhibiting absorption edges of every constituent element of PCMO. Therefore, synchronous monitoring of all absorption edges is possible, as the whole spectral region is recorded in a single pulse. The nitrogen absorption edge derives from the Si_3N_4 sample window.

In PCMO, the melting of the charge-ordered phase leads to a transient metallic phase, characterized by so called "electron-hopping" in a network of Mn^{3+} and Mn^{4+} ions, which are caused by the praseodymium and calcium atoms, respectively.[25] The orbitals involved in this hopping can be monitored through the investigation of the peak at 530 eV, which, amongst others, arises from covalent hybridization between oxygen 2*p* and manganese 3*d* orbitals.[13] Thus, the photo-induced phase transition will be investigated through the absorption changes in the oxygen K edge at 530 eV (Fig. 3, inset).

To illustrate the principle of plasma-based soft-x-ray time-resolved spectroscopy, two NEXAFS spectra of distinguished edge features before and at the illumination through the pump-pulse are shown (Fig. 4). The indicated data point at 530 eV, amongst others, exhibits a decrease in absorption during and after the pump pulse. The temporal evolution of the change in absorption at about 530 eV due to the photo-induced phase transition is shown in Fig. 5.

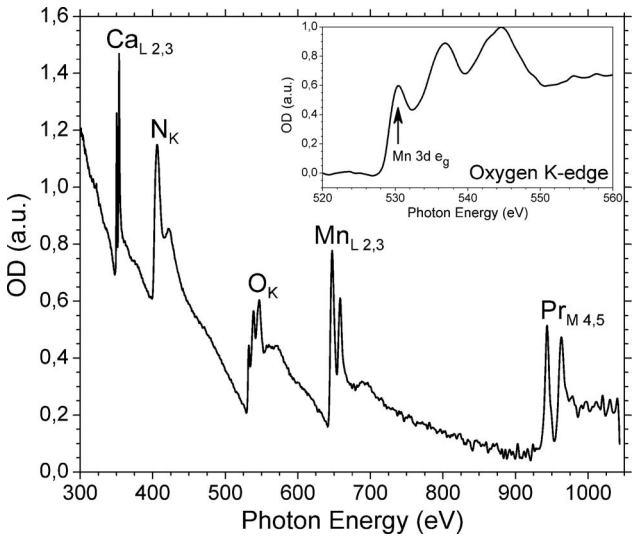

FIG. 3. NEXAFS spectrum of $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) in the water-window region and the section of the oxygen absorption K edge (inset). As can be seen, each element of PCMO has an absorption edge in the water-window. The nitrogen K edge derives from the Si_3N_4 sample window.

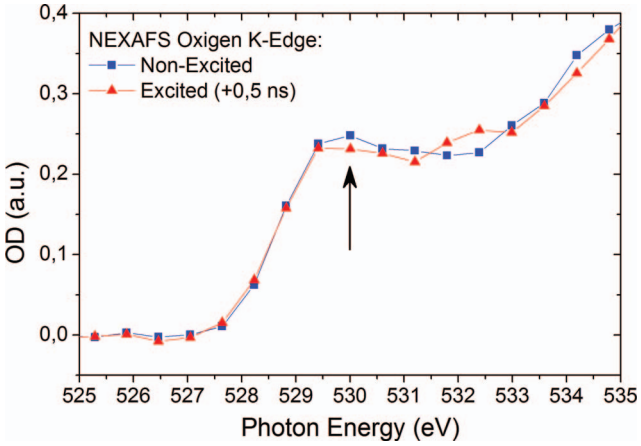

FIG. 4. Static NEXAFS spectra of the oxygen K edge of non-excited PCMO (blue squares) and excited PCMO (red triangles).

At $\Delta t \leq 0.0$ ns, there is basically no change in absorption. For time points with $\Delta t \geq 0.0$ ns the absorption drops, exhibiting a time constant of $\tau = 230$ ps. This is considerably slower in comparison to previously published data ($\tau = 70$ ps by Rini *et al.*[13]), but as with the measurements at a synchrotron radiation source, it reflects the temporal resolution of the given system.

The evolution of the absorption following the photo-induced phase change can be observed very well, even though the static NEXAFS spectra appear to be slightly noisy. The enhancement of the reproducibility by using the laser with a repetition rate of 1 Hz and the calculation of the optical thickness with formula (2) allowed to measure the fairly diminutive changes (about 3.5% change maximum) resulting from the melting of the charge-ordered phase.

While the temporal as well as spectral resolution are considerably lower in comparison to synchrotron-based methods and as the spectral bandwidth is limited to $\lambda = 1$–5 nm, this setup might not be applicable to every scientific question. On the other hand, the amount of change in absorption can be monitored very well and compares to previously published data.[13] For measurements where the temporal evolution of a

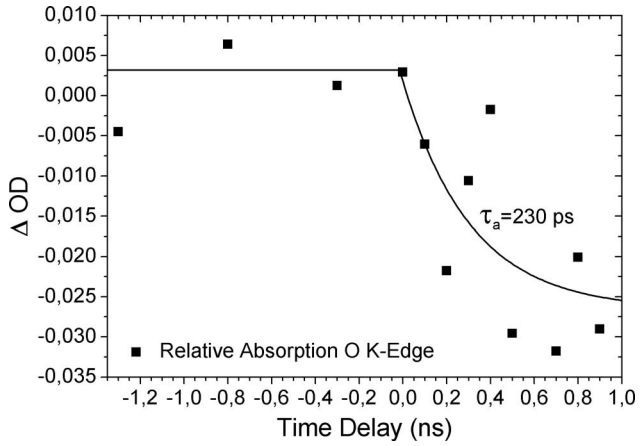

FIG. 5. Relative change in the absorption of the oxygen K edge as a function of the pulse delay at 530 eV due to the photo-induced phase transition. The solid line between time zero and 0.7 ns is an exponential fit of the data points, which yields the temporal resolution of the setup.

given phase change is either of no importance or is slower than the determined 230 ps, this setup yields spectra comparable with synchrotron-based methods, and therefore enables further time-resolved investigations on PCMO and other samples that exhibit equally small or greater changes in absorption after excitation. To enhance further measurements in terms of temporal resolution, a table-top setup based on a laser with a shorter pulse length could be used.

IV. CONCLUSION

Recapitulatory, a table-top soft-x-ray spectrometer based on a ps-laser induced plasma source is introduced, accomplishing time-resolved NEXAFS spectroscopy, as demonstrated for the transient photo-induced phase transition of the CMR manganite $Pr_{0.7}Ca_{0.3}MnO_3$. Absorption changes at the oxygen K edge of 3.5% were observed. This way, the feasibility of conducting time-resolved measurements on liquid nitrogen cooled samples with a temporal resolution or ∼230 ps with a table-top soft-x-ray spectrometer was demonstrated.

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[1]B. Wu and A. Kumar, J. Vac. Sci. Technol. B **25**, 1743–1761 (2007).
[2]I. C. E. Turcu, C. M. Mann, S. W. Moon, and R. Allott, Microelectron. Eng. **35**, 541–544 (1997).
[3]W. Chao, B. D. Harteneck, J. A. Liddle, E. H. Anderson, and D. Attwood, Nature (London) **435**, 1210–1213 (2005).
[4]H. Stollberg, P. Guttmann, P. A. C. Takman, and H. M. Hertz, J. Microsc. **225**, 80–87 (2007).
[5]P. A. C. Takman, H. Stollberg, G. A. Johansson, A. Holmberg, M. Lindblom, and H. M. Hertz, J. Microsc. **226**, 175–181 (2007).
[6]A. Braun, A. Kubatova, S. Wirick, and S. B. Mun, J. Electron Spectrosc. Relat. Phenom. **170**, 42–48 (2009).
[7]O. Dhez, H. W. Ade, and S. G. Urquhart, J. Electron Spectrosc. Relat. Phenom. **128**, 85–96 (2003).
[8]R. K. Hocking, S. DeBeer George, K. N. Raymond, K. O. Hodgson, B. Hedman, and E. I. Solomon, J. Am. Chem. Soc. **132**, 4006–4015 (2010).
[9]C. Peth, F. Barkusky, and K. Mann, J. Phys. D **41**, 105202 (2008).
[10]W. Quevedo, C. Peth, G. Busse, M. Scholz, K. Mann, and S. Techert, Int. J. Mol. Sci. **10**, 4754–4771 (2009).
[11]W. Quevedo, C. Peth, G. Busse, K. Mann, and S. Techert, J. Phys. Chem. B **114**, 8593–8599 (2010).
[12]C. Peth, XUV-Laserplasmaquellen Für Die Absorptions-Spektroskopie Und Zeitaufgelöste Röntgenbeugung, Georg-August-Universität Göttingen, 2008.
[13]M. Rini, Y. Zhu, S. Wall, R. Tobey, H. Ehrke, T. Garl, J. W. Freeland, Y. Tomioka, Y. Tokura, A. Cavalleri, and R. Schoenlein, Phys. Rev. B **80**, 1–5 (2009).
[14]M. Zimmermann, J. Hill, D. Gibbs, M. Blume, D. Casa, B. Keimer, Y. Murakami, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **83**, 4872–4875 (1999).
[15]M. Zimmermann, C. Nelson, Y.-J. Kim, J. Hill, D. Gibbs, H. Nakao, Y. Wakabayashi, Y. Murakami, Y. Tokura, Y. Tomioka, T. Arima, C.-C. Kao, D. Casa, C. Venkataraman, and T. Gog, Phys. Rev. B **64**, 1–9 (2001).
[16]Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, Phys. Rev. B **53**, 1689–1692 (1996).
[17]E. B. Saloman, J. Phys. Chem. Ref. Data **36**, 215–386 (2007).
[18]T. Shirai and K. Okazaki, J. Phys. Chem. Ref. Data **24**, 1577–1608 (1995).
[19]D. Proch and T. Trickl, Rev. Sci. Instrum. **60**, 713–716 (1989).
[20]D. Polli, M. Rini, S. Wall, R. W. Schoenlein, Y. Tomioka, Y. Tokura, G. Cerullo, and A. Cavalleri, Nature Mater. **6**, 643–647 (2007).
[21]H. Nesbitt and D. Banerjee, Am. Mineral. **83**, 305–315 (1998).
[22]D. S. Kim, C. E. Lee, Y. H. Kim, and Y. T. Kim, J. Appl. Phys. **100**, 093901 (2006).
[23]D. Hsu, A. Mani, C. H. Chuang, C. H. Chen, M.-T. Lin, and J. G. Lin, J. Appl. Phys. **105**, 07D505 (2009).
[24]M. Frerichs and F. Voigts, Appl. Surf. Sci. **253**, 950–958 (2006).
[25]M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039–1263 (1998).