A detailed view of an ultrafast phase transition using femtosecond resonant x-ray diffraction

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Abstract: We apply time-resolved resonant x-ray diffraction near the Mn *K*-edge to directly measure the structural and electronic long-range order changes during ultrafast melting of the charge and orbitally ordered phase in a perovskite manganite.
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1. Introduction

The exploration of the subtle interaction of structural and electronic degrees of freedom in strongly correlated electron systems on the femtosecond time scale is an emerging area of research. One goal of these studies is to advance our understanding of the underlying correlations, another is to find ways to control on an ultrafast time scale the technological relevant properties of these materials. Perovskite-type manganites exhibit properties such as colossal magnetoresistance and insulator-to-metal transitions that have significant potential for technological applications**.** These properties are inextricably related to symmetry changes of the atomic lattice and to fascinating ordering patterns of the spins, orbitals and charges [1,2]. Much progress has been made in understanding the various ordering schemes in the adiabatic limit, but little is known about the interactions among the various degrees of freedom. Probing photo-doped manganites using optical methods indicates that the change of electronic properties occurs on a time scale comparable to the period of the Jahn-Teller mode of ~70 fs [3,4]. In contrast employing femtosecond x-ray diffraction (XRD) it was shown with ~200 fs time resolution that the structural rearrangement takes place on a somewhat slower but still non-thermal time scale [5]. Here we take advantage of a free electron laser (FEL) that delivers x-ray pulses of ~50 fs duration and sufficient x-ray flux to measure the very weak superlattice Bragg reflections that become sensitive to the electronic order when the x-ray energy is tuned to the Mn *K* edge.

2. Experimentals

The time-resolved diffraction experiment has been performed at the X-ray Pump-Probe (XPP) instrument at the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory [8]. The sample was excited with 55 fs 800 nm optical pulses at a repetition rate of 120 Hz. An asymmetric diffraction configuration was used to probe the laser induced structural changes. The energy of the x-ray probe pulses was tuned in the vicinity of the Mn *K*-edge using a silicon (111) monochromator. The intensity fluctuations of the monochromatized x-rays and the timing jitter between laser and FEL pulses were measured for each shot. Rebinning the data using this information results in an overall experimental time resolution of ~80 fs**.**

Bragg reflections mainly sensitive to orbital and charge order are reflections with indices of (0 *k*/2 0) and (0 *k* 0), respectively (*k* odd and *pbnm* notation) [6]. To access these reflections we employ a 40 nm thin (011)-oriented $Pr_{0.5}Ca_{0.5}MnO_3$ film grown on (011)-oriented $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) [7]. During the experiments a cryogenic nitrogen blower was used to keep the sample temperature at 100 K well below $T_{CO/OO}$ = 240 K.

3. Results and Discussion

Time-resolved XRD transients for two pump fluences are compared in Figure 1 for two superlattice reflections. The $(\bar{2}\ ½\ 0)$ Bragg reflection measured off resonance is sensititive to the structural dynamics, whereas the $(0\ \bar{3}\ 0)$ senses at resonance mainly the charge order. At low fluences the observed structural dynamics are dominated by a

optical phonon mode of ~2.5 THz which is the slowest of a series of coherent optical phonon modes observed when these materials are excited with very short optical pulses [9]. The $(0\,\bar{3}\,0)$ reflection shows only small modulations.

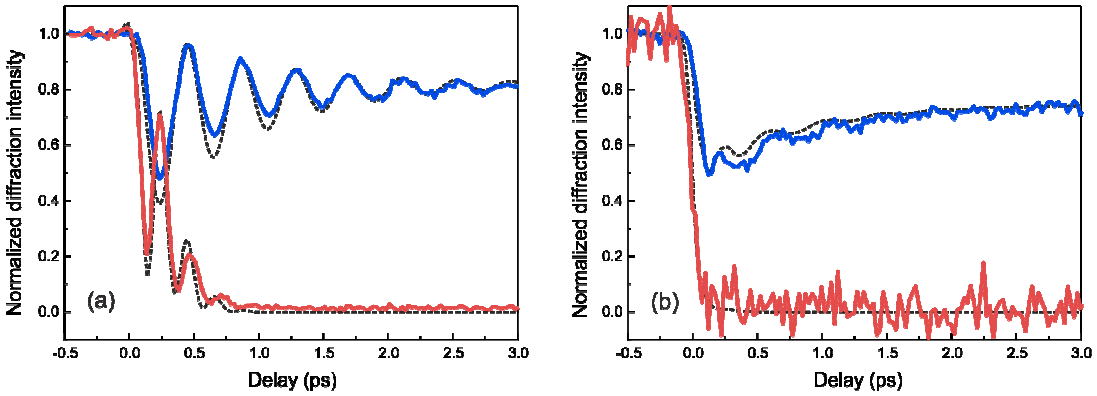

Fig. 1. Time dependent intensity of **(a)** the $(\bar{2}\,½\,0)$ superlattice reflection measured at 6.53 keV and **(b)** the $(0\,\bar{3}\,0)$ reflection measured at 6.555 keV for a pump fluence of 1.8 (blue) and 9.9 mJ/cm^2 (red), respectively. Dashed black lines: simulation based on a single time dependent order parameter. The simulation does not account for the significant resonant enhancement of the $(0\,\bar{3}\,0)$ reflection due to charge order.

At the highest fluences the lattice is immediately driven towards the higher symmetry configuration. The disappearance of the superlattice reflections at high pump fluences is an unambiguous evidence that an increase of symmetry has occurred. The observed doubling of the oscillation frequency in the diffracted signal for the structural $(\bar{2}\,½\,0)$ reflection is an additional sign that the structural symmetry has changed: The atoms are still coherently oscillating with approximately the same frequency but now over their equilibrium positions of the higher symmetry lattice. It takes a couple of damped oscillations for the coherent motions to relax.

Comparing the fluence dependent dynamics of various reflections we will present a scaling model based on a single coordinate describing the underlying order. This model has some similarities to the order parameter concept introduced by Landau and Lifshitz [10]. It describes well the observed structural and electronic dynamics down to a time scale of ~80 fs, the temporal resolution of our experiment.

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