

An ultrafast structural phase transition driven by photo-induced melting of charge and orbital order

In the past decades many new materials with exotic but technologically relevant properties such as high-temperature-superconductivity, colossal-magnetoresistance and multiferroicity have been discovered. These materials, often referred to as "strongly correlated electron systems," exhibit strong coupling between electronic and lattice energy subsystems resulting in a delicate balance between opposing forces. Both impurity doping and external stimuli such as temperature, magnetic or electric fields can induce very large changes in their macroscopic properties. The possibility to control these properties by irradiation with light has opened opportunities to interrogate the underlying correlations in the time-domain using ultrashort optical laser pulses [1-3]. A crucial step, so far missing, is the unambiguous deconvolution of the electronic and structural response of these complex systems. Here we take advantage of the structural information offered by femtosecond hard x-ray diffraction to directly probe the laser-induced structural response of a charge- and orbitally-ordered thin film of $\text{La}_{0.42}\text{Ca}_{0.58}\text{MnO}_3$ after excitation with an intense near-IR laser pulse.

At room temperature $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) is paramagnetic and upon cooling undergoes an insulator-metal transition to a ferromagnetic state for x in the range from 0.17 to 0.5. For $x > 0.5$ the low temperature (T) phase remains insulating with an antiferromagnetic ground state but exhibits charge and orbital order. Figure 1(a) illustrates the monoclinic ground state structure of $P2_1/m$ symmetry for $x = 0.5$ [4]. The low- T phase is stabilized by the Jahn-Teller (J-T) effect that distorts the O octahedra around the Mn^{3+} cations. The structural phase transition to the orthorhombic lattice of $Pbnm$ symmetry at $T > T_{\text{CO/OO}}$ results in a bisection of the unit cell in the direction of the b axis. Although the forces which drive the phase transition are expected to derive from the J-T effect at the Mn^{3+} sites, the major structural component of the phase transition within the unit cell can be described by a shift along the crystal a axis of the Mn^{4+} (with the surrounding octahedral O_6 cage) and of the La/Ca atomic positions.

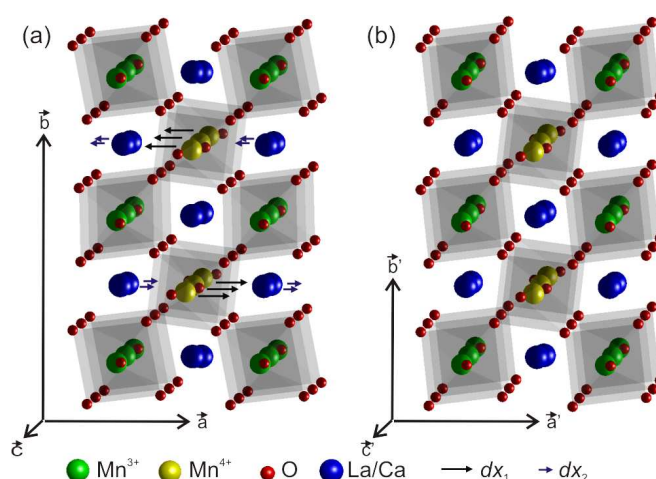


Figure 1: (a) Ground state at 20 K and (b) room temperature structure of half-doped LCMO. Arrows indicate magnified by a factor 10 the atomic motion in the direction of the a axis predominantly responsible for the change of structural symmetry.

The time-resolved diffraction experiments were performed with a grazing incidence geometry using 140 fs x-ray pulses provided by the SLS FEMTO facility [5]. At low excitation fluence (see Figure 2) we observe the displacive excitation of a coherent A_g phonon consistent with the results inferred from previous optical measurements [6]. Under high excitation conditions we observe the sudden drop of a superlattice (SL) reflection that exists only in the charge- and orbitally ordered phase. At the highest fluence the SL reflection then completely vanishes

within 1 ps demonstrating unequivocally that a change of structural symmetry has occurred on a sub-picosecond time scale. The initial step of this phase transition is significantly faster than the temporal experimental resolution of approximately 200 fs. The onset of the phase transition is attributed to the immediate release of the Jahn-Teller (J-T) distortion of the oxygen octahedra at the Mn^{3+} sites promptly triggering the motion of the Mn^{4+} octahedra along the a -direction (see Figure 1) which causes the abrupt drop of the SL peak intensity. To complete the phase transition the La/Ca atoms must adapt to their new equilibrium position. This occurs on a slower time scale due to the weaker Coulomb forces acting on the La/Ca cations.

For fluences below $\sim 2 \text{ mJ/cm}^2$ our data suggest that the nominal Mn^{3+} sites remain distorted on a short subpicosecond time scale, but charge and orbital order is partially disordered. This disordering of the charge and orbital order will cause small changes in the Coulomb field acting on the La/Ca sites which could drive the small displacements observed.

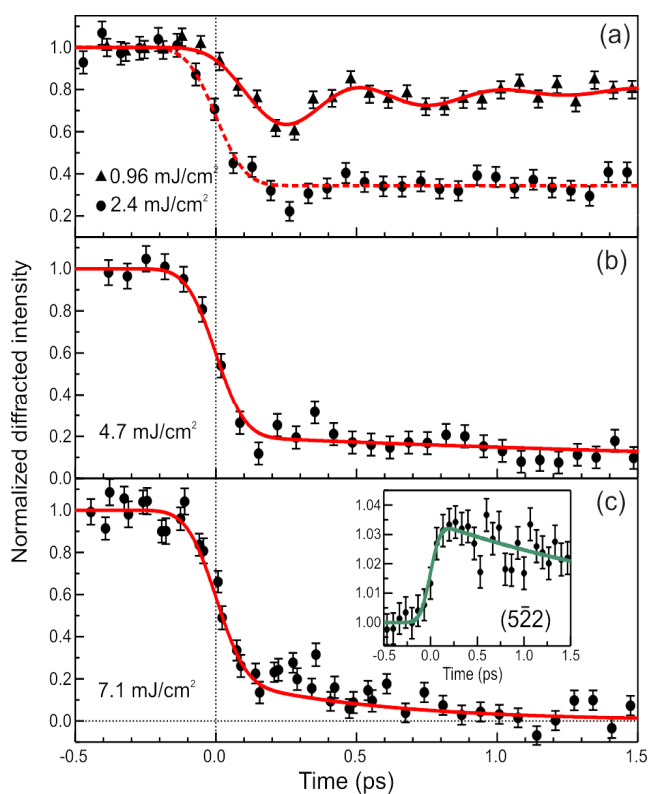


Figure 2: Time dependence (a)–(c) of the normalized diffracted intensity of the SL reflection are shown for several pump fluences. Inset: measured dynamics of the non-SL (5-22) reflection, which during the phase transition should increase by approximately 5%.

References

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Publications

- **An ultrafast structural phase transition driven by photo-induced melting of charge and orbital order**
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