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Photoinduced melting of the orbital order in $La_{0.5}Sr_{1.5}MnO_4$ measured with 4-*fs* laser pulses

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By measuring time-dependent optical birefringence with 4-femtosecond (fs) laser pulses, we determine the time scale for photoinduced melting of orbital order in the single-layer manganite $La_{0.5}Sr_{1.5}MnO_4$. Such high time resolution is required to distinguish atomic motions that control the Jahn-Teller distortion from even faster electronic rearrangements. The experiment reveals an 18 fs bottleneck for the loss of orbital order, corresponding to about one-quarter period of the in-plane Jahn-Teller mode. Furthermore, we observe coherent oscillations of this Jahn-Teller mode. Both their amplitude and the birefringence drop exhibit a threshold in their fluence dependence, indicating cooperativity in the lattice response.

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Materials with strong electronic correlations are characterized by the complex interplay of many microscopic degrees of freedom, including charges, spins, orbitals, and the lattice.[1] Phase transitions in these materials are typically controlled by quasiequilibrium changes in temperature, pressure, or magnetic fields, but they can also be triggered by photostimulation.

Ultrafast photoinduced switching of electronic,[2,3] structural,[4] magnetic,[5] and orbital ordering[6] have been demonstrated. The time scale for photoinduced changes can be used to establish the role of individual degrees of freedom, as demonstrated in optical experiments for the photoinduced insulator metal transition in VO_2,[7] coherent electronic phenomena in manganites,[8,9] or in organic Mott insulators.[10] More recently, time- and angle-resolved XUV photoemission has been used to distinguish electronic and structural processes in the case of charge-density-wave forming materials.[11–13]

In this paper, we identify the elementary time scale for the melting of orbital order in $La_{0.5}Sr_{1.5}MnO_4$, a half-doped single-layered manganite often used as a prototypical example for the microscopic competitions that underpin colossal magnetoresistance.[14–16] Below $T_{CO/OO} = 220$ K, $La_{0.5}Sr_{1.5}MnO_4$ undergoes a simultaneous transition to an in-plane charge- and orbital-ordered (CO/OO) state, with three-dimensional antiferromagnetism setting in below $T_N = 110$ K.[17,18] The charges order in a checkerboard pattern with alternating Mn^{3+} and Mn^{4+} sites, as shown in Fig. 1(a). The Mn 3*d* orbitals form *zigzag* chains along the $(1\bar{1}0)$ crystallographic direction, involving simultaneous energy gains from a Jahn-Teller distortion and from the superexchange interaction.[19]

Photoexcitation of $La_{0.5}Sr_{1.5}MnO_4$ has also been shown to trigger a reduction in orbital and magnetic order,[6,20] although the time resolution in these experiments was not sufficient to differentiate between structural and electronic effects. One of the challenges for such a determination is that the Jahn-Teller distortion exhibits a typical period of only $T_{JT} = 60$–70 fs. Therefore, a time resolution significantly below $T_{JT}/4 = 15$–18 fs is required to evidence the existence of a "structural bottleneck" in this type of photoinduced phase transition.

For the experiments reported in this paper, a crystal of $La_{0.5}Sr_{1.5}MnO_4$ was grown using the floating zone method and cleaved along the *ab* planes. The doubling of the square unit cell along the *b* axis (see Fig. 1) causes a finite optical birefringence signal, which quantitatively tracks the order parameter.[21] We performed optical pump, birefringence probe experiments using an amplified Ti:sapphire laser, which, in combination with a hollow core fiber and chirped mirror compression, was used to generate ∼4 fs pulses at a 3 kHz repetition rate.[22,23] These laser pulses are centered around 1.7 eV photon energy with a usable bandwidth of about 1.0 eV, thus being located within the broad $Mn^{3+} \rightarrow Mn^{4+}$ (e_g) charge-transfer band peaking at 1.3 eV.[6,21] To preserve the short laser pulse duration in the experiment, partial reflection of the beam at the edge of a D-shaped mirror was used to split the light into a pump and probe. A concave mirror was used for focusing on the sample. The pump beam, with an 80-μm-diam spot size, was incident normal to the sample surface. The probe beam (40 μm spot size on the sample) was spatially overlapped with the pump beam at an angle of about 10°. The polarization of the pump pulse was aligned along the diagonal of the *ab* surface, thus preferentially exciting charge transfers along the ferromagnetic chain depicted in Fig. 1. The time-dependent change in optical birefringence ($\Delta B/B$) was probed at 700 nm (1.77 eV), recorded by filtering the broadband spectrum of the 4-fs pulse after reflection from the sample to preserve the time resolution to the limit of the ultrashort pulse duration. The experiments were performed at a temperature of 20 K, well below $T_{CO/OO}$ and T_N.

Figure 2 shows photoinduced changes of the in-plane optical birefringence for different pump fluences. The optical birefringence drops promptly after excitation, decreases further on the 100 fs time scale, and partially recovers to a long-lived state. A superimposed oscillatory response is also observed, at both positive and negative time delays, the latter being an experimental artifact as described later.

Figure 3 zooms into the large drop in birefringence $\Delta B/B$ within the first 50 fs after photoexcitation with pulses of 2.7 mJ/cm^2 fluence. An autocorrelation trace of the ∼4 fs full width at half-maximum laser pulses [red dashed line, obtained using a transient grating frequency-resolved optical gating

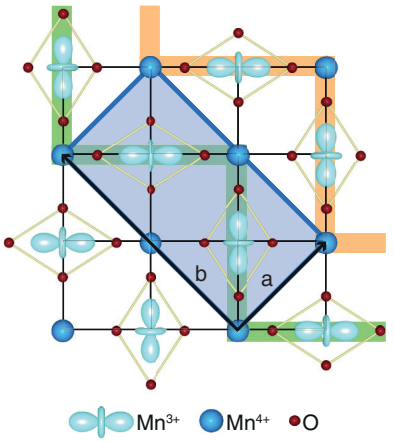

FIG. 1. (Color) Schematic picture of charge-orbital ordering in the *ab* plane of $La_{0.5}Sr_{1.5}MnO_4$: the checkerboard-type pattern of Mn^{3+} and Mn^{4+} ions is accompanied by zigzag chains of e_g orbitals on the Mn^{3+} sites (thick yellow and green lines). The orbital ordering and the accompanying Jahn-Teller distortions result in the formation a rectangular unit cell (blue rectangle) and optical anisotropy.

(FROG)] and its temporal integral (red solid line) are also reported on the same plot. The most important observation is that the loss of optical birefringence proceeds on a time scale significantly longer than the pulse or its time integral, thus indicating the existence of a bottleneck in the photoinduced dynamics. This is quantified by the error function fit (blue solid line, as also shown in Fig. 3), which yields a signal drop time of 18 fs.

This time scale correlates well with that of the oscillatory response superimposed on the signal. These oscillations were isolated from the curves shown in Fig. 2 by subtracting a fit to the nonoscillatory signal components, i.e., an error function rise and further exponential growth and recovery shown as thin solid lines. The oscillations at negative time delays are a well-known artifact of pump-probe spectroscopy, observed when the pump and probe pulse durations are short compared

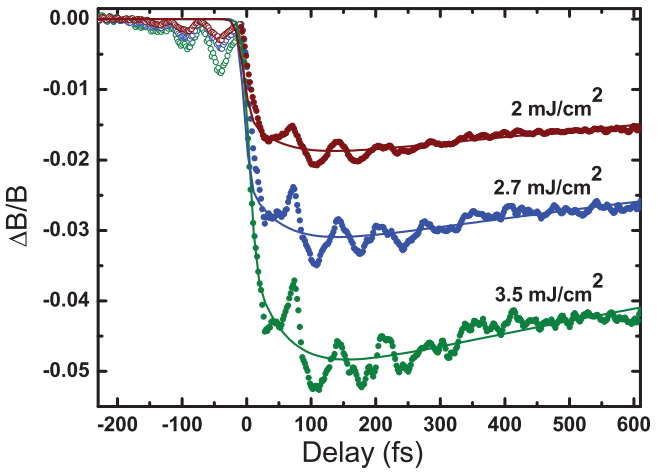

FIG. 2. (Color) Change in birefringence in the MnO_2 plane as a function of pump-probe delay time at a sample temperature of 20 K for different pump fluence. Solid lines are fit to the data as described in the text.

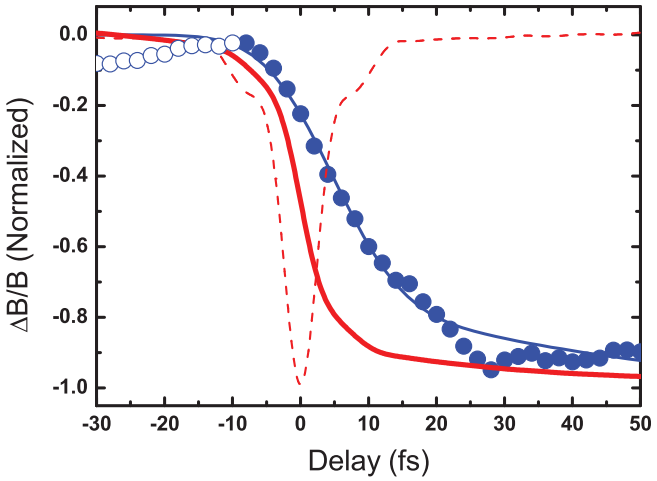

FIG. 3. (Color) Zoom into the rising edge of the birefringence signal at a pump fluence of 2.7 mJ/cm^2, as shown in Fig. 2. The blue solid line shows an error function fit to the rising edge. The autocorrelation of ∼4 fs laser pulse is shown as a red dashed line, together with its temporal integral (solid).

to dephasing times.[24–26] This effect, typically referred to as *perturbed free-induction decay*, carries no physical information. The oscillations at positive time delays are shown in the inset of Fig. 3(a), along with their Fourier transformation. The frequency of 14.7 THz and the corresponding period of 68 fs are in close agreement with the frequency and period of the in-plane B_{1g} Jahn-Teller mode in $La_{0.5}Sr_{1.5}MnO_4$, as known from continuous-wave Raman scattering.[27]

Two important effects can be extracted by comparing the loss of optical birefringence and the coherent oscillations. First of all, the 18 fs bottleneck time scale measured in Fig. 2 is approximately one-quarter of the full Jahn-Teller period, underscoring a picture in which the melting of orbital order occurs along the physical pathway of a coherent Jahn-Teller motion. Secondly, when analyzing the fluence dependence of the orbital order melting, we find that the peak amplitude of the photoinduced birefringence [Fig. 4(b)] and the coherent B_{1g} phonon amplitude [see Fig. 4(c)] scale very similarly. Importantly, a threshold of about 1 mJ/cm^2 (Ref. 8) is observed, a general feature for light-induced phase transitions[4,7,8,28,29] but not of optically excited coherent phonons. In fact, coherent oscillations are typically excited by the conventional impulsive Raman mechanism[30,31] and scale linearly with fluence without a threshold. However, the present observation of the threshold in the fluence-dependent coherent phonon amplitudes allows us to conclude that the coherent motions are triggered by a cooperative lattice-orbital response above a sufficiently high photodoping level.

This experiment suggests the following physical picture for the ultrafast melting of orbital order in $La_{0.5}Sr_{1.5}MnO_4$. Charge-transfer excitations along the ferromagnetic chain redistribute charges along the ground-state orbital pattern, triggering a cooperative Jahn-Teller rearrangement, which in turn drives the reduction in orbital order. Importantly, the motion of the lattice and the loss of orbital order both appear to proceed along a cooperative pathway, with a fluence threshold that is not observed in more conventional

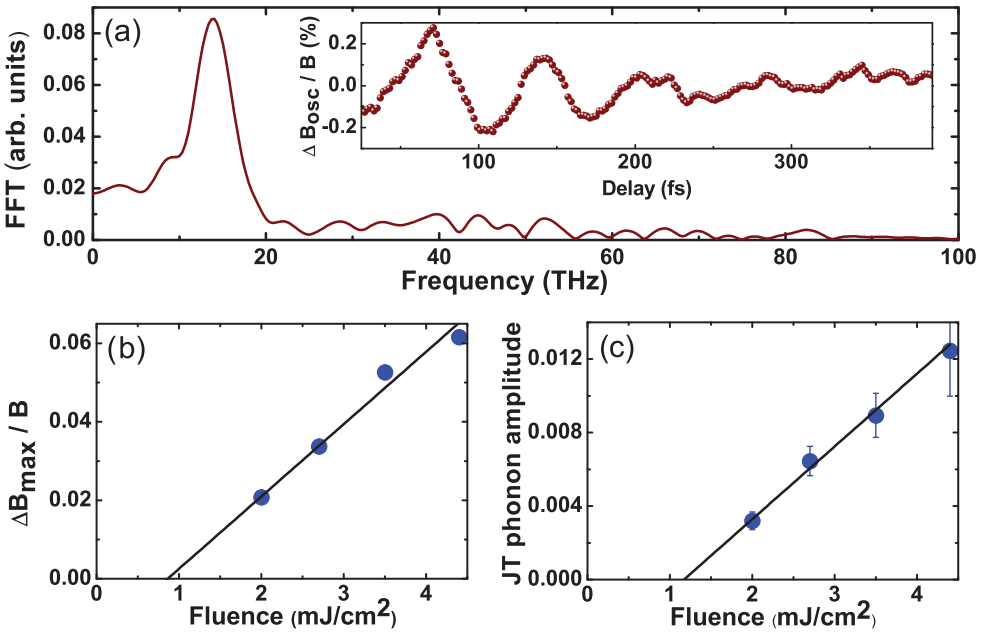

FIG. 4. (Color) (a) Oscillations isolated from the time profile of $\Delta B/B$ for positive time delays, shown in the inset, together with its Fourier transformation. Fluence-dependent amplitudes of (b) the transient birefringence signal and (c) the coherent phonon oscillations of the Jahn-Teller mode. Solid lines in (b) and (c) are linear fits to the data.

Raman-based excitations. Time-resolved x-ray diffraction experiments on Jahn-Teller sensitive superlattice reflections may help to investigate the detailed atomic motions connected to the light-induced orbital order melting.[32]

In summary, time-resolved optical birefringence measurements with extreme (4 fs) time resolution allow for a determination of a temporal bottleneck in the photoinduced orbital melting in $La_{0.5}Sr_{1.5}MnO_4$. Evidence for a cooperative lattice, i.e., orbital response, as determined by the fluence dependence of the coherent atomic structural motions, substantiates a picture in which photoinduced rearrangements of orbital order in $La_{0.5}Sr_{1.5}MnO_4$ are to be viewed as a structural rather than electronic process. More generally, our data suggest that the existence of a structural distortion, rather than the superexchange interaction, is the key ingredient in the stabilization of the orbitally ordered ground state. This experiment also establishes the importance of ever shorter time scales for measurements of this kind, underscoring the importance of few-femtosecond pulse durations to study nonequilibrium dynamics in complex oxides.

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