Photocreating supercooled spiral-spin states in a multiferroic manganite

Y. M. Sheu,1,2,* N. Ogawa,2 Y. Kaneko,2 and Y. Tokura2,3

1Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan
2RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan
3Department of Applied Physics and Quantum-Phase Electronics Center (QPEC), University of Tokyo, Tokyo 113-8656, Japan

(Received 16 December 2015; revised manuscript received 24 February 2016; published 18 August 2016)

We demonstrate that the dynamics of the ab-spiral-spiral order in a magnetoelectric multiferroic Eu0.55Y0.45MnO3 can be unambiguously probed through optical second harmonic signals, generated via spin-induced ferroelectric polarization. In the case of weak excitation, the ferroelectric and the spiral-spiral order remains interlocked, both relaxing through spin-lattice relaxation in the nonequilibrium state. When the additional optical pulse illuminating the sample is intense enough to induce a local phase transition thermally, the system creates a metastable state of the bc-spiral-spiral order (with the electric polarization $P \parallel c$) via supercooling across the first-order phase transition between the $ab$ and $bc$ spiral. The supercooled state of the $bc$-spiral spin is formed in the thermodynamical ground state of the $ab$ spiral ($P \parallel a$), displaying a prolonged lifetime with strong dependence on the magnetic field along the $a$ axis. The observed phenomena provide a different paradigm for photoswitching between the two distinct multiferroic states, motivating further research into a direct observation of the photocreated supercooled $bc$-spiral spin in multiferroic manganites.

DOI: 10.1103/PhysRevB.94.081107

Spin kinetics via light-matter interactions has been of great interest ever since the discovery of ultrafast demagnetization in a ferromagnetic metal [1]. The exchange interaction, spin-orbit interaction, and spin precession are believed to dominate spin relaxation after photoexcitation [2]. The recent development of spin-induced magnetoelectric (ME) multiferroics [3–7] brings up substantial questions about the photoinduced dynamics due to more delicate interactions. ME multiferroics of a spiral-spiral spin origin can lead to cross correlations between ferroelectric (FE) and spiral-spiral orders, since the ionic displacement is a direct consequence of the inverse Dzyaloshinskii-Moriya (DM) interaction [8,9]. The spin dynamics of ME multiferroics has been a subject of scrutiny [5,10–13] as it may become the platform for ME memory [14]. Although insight into the dynamical spiral-spiral response has been given by using resonance THz or ac electric fields [10–13,15,16], a comprehensive understanding of ME dynamics is still lacking, primarily due to the lack of direct access to the FE order on various time scales [17,18]. However, their influence could be significant and unexpected states might be accessible from couplings between different degrees of freedom (DOF) in nonequilibrium cases. Therefore, we aim to unveil the photoexcited dynamics of spiral-spiral-induced ME coupling.

Multiferroic perovskite manganites, $RMnO_3$ [$R$ being Tb, Dy, (Eu,Y), etc.], possess either $ab$- or $bc$-plane spin-spiral states (abbreviated as $ab$ spiral and $bc$ spiral) with the propagation wave vector $k$ along the $b$ axis [Fig. 1(a)]. The two spiral states give rise to FE polarization, $P \parallel a$ or $P \parallel c$, respectively, through the inverse DM interaction [8,9,19]. An external magnetic field ($B$) changes the axis of the spin cone, flipping between the $ab$ spiral (under $B \parallel c$) and the $bc$ spiral (under $B \parallel a$) through a first-order phase transition (1stPT) [20] [Fig. 1(b)].

To explore the photoinduced phenomena of the two distinct ME states in perovskite manganites, we utilize the spin-induced FE polarization of Eu0.55Y0.45MnO3 (EYMO) to produce second harmonic generation (SHG). SHG has been frequently applied to multiferroics of a spiral-spiral origin, such as MnWO4 [15,21–23], TbMnO3 [24], TbMn2O3 [16], and CuO [25]. The techniques have been reviewed in depth [26,27]. Time-resolved SHG (TR-SHG) can directly access the FE polarization (or, equivalently, the spiral-spiral order here), spanning a wide range of time scales [15,28–30]. Time-resolved research is practical for tracing the dynamics of various DOF [6,30–36]. Besides, the capability of generating highly nonequilibrated states with ultrashort pulses may lead to the discovery of hidden states [37–39], which would not be realized through conventional thermodynamic processes.

Single crystals EYMO of orthorhombic perovskite were grown by the floating zone method. The $ac$ surface was mechanically polished to ~1 mm thickness, and annealed at 750 °C in air for 12 h to reduce the residual strain. It was mounted in a cryostat with a superconducting magnet and in contact with exchange He gas, allowing for a significant reduction in cooling time of the sample, especially when heated by laser pulses.

Our TR-SHG experiments are based on an amplified Ti:sapphire laser system (1 kHz and ~120 fs centered at 800 nm). Photon energies ($E_{ph}$) of 0.48–1.12 eV are generated by optical parametric amplifiers. The SHG signal is detected by a photomultiplier tube using lock-in techniques after filtering out the fundamental photon. A combination of an optical chopper and a mechanical shutter is employed for the long-time-delay measurements. All measurements are performed under zero field cooling.

At low temperature ($T$), EYMO has an $ab$-spiral ground state ($P \parallel a$), of which the free-energy landscape is illustrated by the left inset of Fig. 1(b). As $T$ rises, the $bc$ spiral becomes thermodynamically more stable. The 1stPT between the two spin-spiral states occurs around 21 K, above which the FE polarization rotates to along the $c$ axis [20,41]. At 6 K without $B$, the polar plot of $p$-polarized ($\parallel a$) and $s$-polarized ($\parallel c$)
The phase transitions from the 0.77 eV corresponds to 4.24 J/cm³ in our data), we observe a gradual reduction in $I_{\text{SHG}}$ as a function of delay time $t$ [Fig. 2(a)]. The photoinduced depolarization is completed around $t \sim 50–100$ ps, and the time constant is independent of $T$, $B$, excitation fluence $E_\text{ph}$ [Figs. 2(a)–2(d)], or light polarization (circular and linear; only the circular is shown). The time constant for $I_{\text{SHG}}$ reduction is within the typical range of spin-lattice (S-L) relaxation in manganites [43–45], in accord with a recent report [17] and our transient reflectivity ($\Delta R/R$) data [42]. It is noted that the $I_{\text{SHG}}$ for $t < 0$ corresponds to the steady-state SHG at 1 ms after an 120 fs pulse excitation and depends on $T$ and $B/a$ [Fig. 1(d)].

Comparing our $\Delta R/R$ with TR-SHG [42], we can conclude that TR-SHG unambiguously probes the spiral-spin dynamics without an electronic contribution to the FE depolarization, due to the lack of a fast electronic response ($<1 \mu$s) in TR-SHG, while it is discerned in $\Delta R/R$. Besides, the insensitivity of TR-SHG to pump $E_\text{ph}$ again implies that the relaxation of spiral spin is not triggered by an electronic contribution from specific optical transitions (including the $d$-$d$ transition here and the $p$-$d$ charge transfer [17]). We can infer that the local spins (of $t_{2g}$ electrons) are still responsible for the FE polarization after an electronic transition and/or transfer of excited $e_g$ electrons, maintaining FE and spin interlock in the nonequilibrium case. Further insights beyond the scope of this Rapid Communication are provided in the Supplemental Material [42].

The lack of an electronic response and the characteristic S-L time constant observed in TR-SHG implies thermal-induced spin depolarization upon photoexcitation. The transient and quasiequilibrium lattice temperature can be deduced from the TR-SHG traces at various $T$‘s [Fig. 2(a)]. At 3 K, using 0.3 $\mu$J pulses ($E_\text{ph} = 0.77$ eV), the estimated change in $T$ ($\Delta T$) is $\sim 9$ K from the reduced magnitude of $I_{\text{SHG}}$. At a fixed fluence, $\Delta T$ reduces with increasing the sample base temperature [Fig. 2(a)], whereas it stays constant upon changing the magnitude of $B \parallel a$ [Fig. 2(b)]. This is reasonably anticipated from the increase of heat capacity at higher $T$. The time constant for the laser-induced-heating process does not depend on the $E_\text{ph}$ ranging from 0.55 to 1.55 eV [Fig. 2(d)]. Furthermore, the insignificant change in relaxation time near the transition indicates the nature of 1stPT, unlike
the critical behavior of spin kinetics in manganites that possess second-order phase transitions [44–46].

Intriguing phenomena are uncovered as the excitation density increases further: Photodepolarization of the spin-induced FE becomes faster and finally the TR-SHG disappears completely [Fig. 3(a)]. To discern its origin, we plot the decay time constant versus excitation energy density in Fig. 3(b), revealing a threshold behavior irrespective of pump $E_{ph}$’s. Above the threshold the TR-SHG goes to zero within 20 ps and remains at zero for a long time (>500 ps), whereas below the threshold TR-SHG never completely reduces to zero, and slow S-L relaxation dominates the FE depolarization, irrespective of sample temperature and magnetic field. Thus the threshold energy density differentiates the “low” and “high” excitation regime, illustrated in the white and gray areas of Fig. 3(b).

As the pump intensity approaches the threshold, a subtle behavior occurs before $t = 0$ [Fig. 2(c)]. We notice a small reduction of $I_{SHG}$, which becomes significant under high excitation [Fig. 3(a)], e.g., $I_{SHG}(t < 0) > I_{SHG}(t < 0)$, indicating incomplete recovery of the $ab$ spiral within 1 ms and signaling a situation generally not explored in time-resolved optical experiments. The observed reduction is not simply attributable to accumulated lattice thermalization, but rather points to the emergence of metastable spin orders, as discussed below.

To investigate the sudden SHG reduction before $t = 0$ (i.e., existing at 1 ms after photoexcitation), we reduced the pump repetition rate to allow the system to recover the thermodynamic ground state ($ab$ spiral) at the base temperature. We also adjust the pump intensity around 24–28 $\mu$J to unveil the dynamics of the metastable state. The resultant SHG traces at various $T$’s [Fig. 4(a)] and under different $B \parallel a$ [Fig. 4(b)] reveal a dramatic change in the recovery time, spanning from a few seconds up to several minutes. As the base temperature approaches the phase transition, the recovery time becomes longer [Fig. 4(a)]. Similarly, the application of $B \parallel a$ lengthens the recovery time [Fig. 4(b)]. We thus exclude the lattice residual heating as the origin of SHG reduction, since it would not have a strong dependence on the base temperature nor the applied $B$ field. Because $B \parallel a$ energetically favors the $bc$ spiral and the (thermal) recovery inevitably goes through the phase of the $bc$ spiral, the prolonged response after the intense excitation likely involves the transition of the photogenerated $bc$ spiral to the original $ab$ spiral.

As the pump intensity approaches the threshold, a subtle behavior occurs before $t = 0$ [Fig. 2(c)]. We notice a small reduction of $I_{SHG}$, which becomes significant under high excitation [Fig. 3(a)], e.g., $I_{SHG}(t < 0) > I_{SHG}(t < 0)$, indicating incomplete recovery of the $ab$ spiral within 1 ms and signaling a situation generally not explored in time-resolved optical experiments. The observed reduction is not simply attributable to accumulated lattice thermalization, but rather points to the emergence of metastable spin orders, as discussed below.

To investigate the subtle SHG reduction before $t = 0$ (i.e., existing at 1 ms after photoexcitation), we reduced the pump repetition rate to allow the system to recover the thermodynamical ground state ($ab$ spiral) at the base temperature. We also adjust the pump intensity around 24–28 $\mu$J to unveil the dynamics of the metastable state. The resultant SHG traces at various $T$’s [Fig. 4(a)] and under different $B \parallel a$ [Fig. 4(b)] reveal a dramatic change in the recovery time, spanning from a few seconds up to several minutes. As the base temperature approaches the phase transition, the recovery time becomes longer [Fig. 4(a)]. Similarly, the application of $B \parallel a$ lengthens the recovery time [Fig. 4(b)]. We thus exclusion the lattice residual heating as the origin of SHG reduction, since it would not have a strong dependence on the base temperature nor the applied $B$ field. Because $B \parallel a$ energetically favors the $bc$ spiral and the (thermal) recovery inevitably goes through the phase of the $bc$ spiral, the prolonged response after the intense excitation likely involves the transition of the photogenerated $bc$ spiral to the original $ab$ spiral.

**FIG. 3.** Formation of metastable states under high excitation. (a) TR-SHG of $p$-in (1.0 eV) and $p$-out (2.0 eV) setups measured at 1.6 K under various pump intensities (>1 $\mu$J). The vertical arrows indicate the estimated change in lattice temperature. (b) Time constant of FE depolarization vs excitation energy density at three $E_{ph}$’s. The time constant is extracted from the fit of a single exponential decay. The shaded gray area covers the excitation density leading to the complete reduction of the SHG (i.e., phase transition to the $bc$ spiral or higher-$T$ phases). The color block in the inset represent the corresponding lattice temperatures and the respective multiferroic/magnetic phases therein.

**FIG. 4.** Photocreating the metastable $bc$ spiral from the ground state of the $ab$ spiral. The high excitation in the gray area of Fig. 3(b) creates a metastable spin state, which is probed by the long-lived reduction in spin-induced SHG: (a) TR-SHG measured at various temperatures and (b) the corresponding lifetimes of the metastable states. (c) The recovery of photocreated metastable states under application of various $B \parallel a$ at 5 K, and (d) the corresponding lifetimes. The inset illustrates a schematic free-energy landscape against the canting angle of the spin-spiral plane around the $b$ axis and a formation of the metastable $bc$ spiral.
The remarkably long time scale observed here indicates the formation of a metastable state, reachable by supercooling the system through 1stPT, from which a system cannot escape at low enough temperatures due to the high free-energy potential barrier [47,48]. In other words, the supercooled state preserves partially or dominantly the order of high-temperature states, because the time scale to form the critical size of the thermodynamical ground state becomes long enough. We can estimate the cooling rate from the trace of 1 μJ excitation shown in Fig. 2(c). The residual heating of ~4 K is estimated by the SHG signal just before \( t = 0 \), while the transiently elevated temperature \( \Delta T (t > 100 \text{ ps}) \) is ~14 K, implying a cooling rate as high as \( 10^4 \text{ K/s} \) (10 K recovered in 1 ms). The supercooling is often observed in temperature- and/or magnetic-field-hysteresis features of other multiferroics of RMnO\(_3\) [49] and charge-ordered manganites with 1stPTs [50].

We can use this estimate to differentiate between the two processes of SHG reduction, i.e., lattice heating versus the formation of the metastable state. Using a linear extrapolation of the relation between light absorption and heat for the present experimental condition in Fig. 4, we estimate the lattice heating up to ~300 K which cools to the base temperature in ~30 ms after photoexcitation. Here, we neglect the slowdown of thermal transport due to the subsequent heat conduction between interfaces, as our sample is mounted in contact with He exchange gas to achieve better heat relaxation. The recovery time, shown in Figs. 4(b) and 4(d), is nearly four orders of magnitude longer than the lattice cooling time; thus the magnetically ordered phase (e.g., spin spiral) should be restored. We exclude a change in the recovery time arising from the variation in heat diffusion. If it were the case, we would observe a gigantic critical slowing down during S-L relaxation in the low-excitation case [Fig. 2(a) and 2(c)]. Instead, we observe a gigantic critical slowing down during S-L relaxation. If it were the case, we would conclude that the magnetically ordered phase (e.g., spin spiral) should be restored. However, during supercooling across the \( T_c \) of the bc spiral, the application of \( B \parallel a \) can energetically favor the bc spiral to be trapped momentarily as the transient state. Further cooling can barely overcome the potential barrier between the \( ab \) and bc spiral, and the field activated stable phase of the bc spiral cools down and is fixed by the barrier, forming a metastable state at the base temperature [inset of Fig. 4(d)]. Therefore, when the sample is near \( T_c \) or under \( B \parallel a \), the bc spiral is dominant more than other collinear sinusoidal or disorder states during supercooling. Future investigations of the photocreared supercooled state from a direct \( bc \)-spiral signal may help to gain deeper insight. Finally, we note that within the model of the supercooled \( bc \) spiral, the peaklike feature near \( t = 0 \) for excitation >4 μJ in Fig. 3(a) could be understood as repumping the thermodynamically unfavorable metastable state at 1 kHz. Complicated mixtures of excitation could be involved. Experimentally, it disappears upon reducing the laser repetition rate.

In conclusion, by probing the temporal variation of SHG from the spiral-spin-induced FE polarization, we have investigated the dynamics of photoexcited multiferroic EYMO, spanning a time scale from \( 10^{-12} \) to \( 10^3 \) s. We confirm that there is no specific electronic contribution to FE depolarization apart from the thermalization due to spin-lattice relaxation on all time scales. We find that a metastable \( bc \) spiral (\( P \parallel c \)) can be photocrated from the \( ab \) spiral (\( P \parallel a \)) through supercooling from the photothermalyzed state. We observe the two distinct dynamics differentiated by a threshold energy density of photoexcitation: Below the threshold the spiral spin relaxes through S-L coupling and the whole system cools back to the base temperature while preserving \( P \parallel a \). Contrarily, above the threshold, we observe a remarkably slow SHG recovery with a strong dependence on temperature and magnetic field along the \( a \) axis. This feature, together with the estimated cooling rate, allows us to conclude that the formation of the metastable \( bc \) spiral (\( P \parallel c \)) is feasible through supercooling multiferroic manganites upon femtosecond-laser excitation. Our study provides deep insight into the switch of multiferroics of a spiral-spin origin and will pave a different avenue toward nonvolatile memory-storage functionality [39].

The authors thank F. Kagawa for stimulating discussions and M. Ishida for technical help. This research is granted by the JSPS Grant-in-Aid for Scientific Research(S) No. 24224009. Y.M.S. acknowledge the support from the Taiwan Ministry of Science and Technology, Grant No. MOST 104-2112-M-009-023-MY3.
