Coherent acoustic phonons in hexagonal manganite LuMnO$_3$

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We have observed coherent acoustic phonons in the hexagonal manganite LuMnO$_3$ using two-color femtosecond optical pump-probe spectroscopy. The dependence of the oscillatory component of the photoinduced reflectivity on the probe wavelength and incident angle is consistent with a propagating strain pulse. Moreover, the frequency, dephasing, and phase of the oscillation are found to be temperature dependent. In particular, a large phase shift occurs in the vicinity of the Néel temperature ($T_N$), which we relate to the temperature-dependent on-site Mn $d$-$d$ transition that is coupled to antiferromagnetic ordering, as recently observed in optical conductivity measurements.


Optical spectroscopy has proven a useful tool in helping to unravel the competition between charge, orbital, lattice, and spin degrees of freedom in technologically relevant doped transition-metal oxides and their undoped parent compounds. Recently, there has been renewed interest in hexagonal manganites ($RMnO_3$, $R$ = Lu, Y, for example) because of their multiferroic behavior and potential for electrically and optically controlling their magnetic properties. Recent optical conductivity measurements show a blueshift of the on-site Mn $d$-$d$ transition with decreasing temperature consistent with short-range spin correlations in this strongly frustrated antiferromagnet ($T_N \approx 90$ K).

Femtosecond optical spectroscopy complements these more conventional optical methods since electron, phonon, and spin dynamics can be directly resolved in the time domain.$^2$

For example, coherent acoustic phonon oscillations have been observed in many materials, such as semiconductors,$^{3-5}$ semiconductor heterostructures,$^{6-10}$ metals,$^{11,12}$ and colossal magnetoresistive manganites$^{13,14}$ using all-optical pump-probe spectroscopy and, more recently, time-resolved x-ray diffraction.$^{15}$ Several mechanisms of coherent acoustic phonon generation and detection have been proposed. Propagating strain pulses generated by instantaneous thermal strain using pulsed lasers in an opaque sample was first proposed by Thomsen et al.$^{16,17}$ In this case, a periodic oscillation is observed due to self-interference of the reflected probe beam from the crystal surface and the surface defined by the propagating strain pulse. Other generation mechanisms include impulsive stimulated Raman scattering$^{6,7}$ and dissipative excitation of coherent phonons,$^5$ which have been observed in bulk semiconductors and superlattices. In both cases the coherent acoustic oscillations are detected through changes in the reflection or transmission by modulation of the interband transition onset via the acoustic deformation potential. Finally, a large amplitude oscillation in GaN heterostructures has been observed and attributed to the screening of the piezoelectric field by photoexcited carriers.$^9,10$

Here, we report on the generation and detection of coherent acoustic phonons in LuMnO$_3$. Hexagonal manganite LuMnO$_3$ is multiferroic, with a ferroelectric phase transition $T_c \approx 900$ K and an antiferromagnetic (AFM) transition near $T_N \approx 90$ K. It has a well-defined optical conductivity peak at 1.7 eV, which is attributed to an on-site electric dipole allowed Mn $d$-$d$ transition that is coupled to short-range AFM spin fluctuations.$^1$ We have performed time-resolved optical pump-probe spectroscopy on LuMnO$_3$, where we probe the photoinduced changes in reflectance $\Delta R/R$ at energies close to this $d$-$d$ optical transition. We show that photoexcitation generates a propagating strain pulse, giving rise to oscillations in $\Delta R/R$. The oscillation frequency, dephasing time, and phase are temperature dependent. A pronounced phase change occurs in the vicinity of the Néel temperature ($T_N$), which is related to the temperature dependent redshift of the on-site Mn $d$-$d$ optical transition at 1.7 eV that is coupled to the AFM ordering as recently observed in optical conductivity measurements.$^1$

LuMnO$_3$ single crystals were grown by the traveling floating zone method and cleaved into platelet samples with thickness less than 100 μm. Magnetization, resistivity, and x-ray diffraction were measured to confirm the crystal properties. A portion of the 1 KHz regenerative amplifier output with wavelength 800 nm, pulse energy 2.5 mJ, and pulse duration 50 fs, was frequency doubled to provide the 400 nm pump excitation. The tunable, visible probe was obtained by frequency doubling the output of an infrared optical parametric amplifier. The pump-induced change in the reflectance $(\Delta R/R)$ was measured as a function of a pump-probe delay using a mechanical delay line.

In Fig. 1, periodic oscillations in the differential reflectance $\Delta R/R$ are plotted with changing (a) pump wavelength, $\lambda_{\text{pump}}$, (b) probe wavelength, $\lambda_{\text{probe}}$, (c) the incident angle of the probe beam $\theta$, and (d) temperature. The oscillation frequency, dephasing time, and phase of the oscillation do not depend on $\lambda_{\text{pump}}$. In contrast, when $\lambda_{\text{probe}}$ is changed from 800 to 400 nm, the oscillation frequency shows a strong dependence on $\lambda_{\text{probe}}$ [Fig. 1(b)]. Furthermore, as shown in

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els, the oscillation frequency depends on suggests a well-defined oscillation frequency. In both mod-
in the reflectance has the following form: 

\[ R \propto \frac{4 \pi n v_s}{\lambda} \cos \theta - \phi e^{-t/\tau_d} \]  

Here \( \theta \) is the angle of the probe beam with respect to \( z \) axis 
inside the crystal, \( \tau_d \) is dephasing time, and \( \phi \) is the phase.

Fig. 1(c), increasing the angle of \( \theta \) results in an increase in 
the oscillation period. In the case of impulsive stimulated 
Raman scattering, the generated acoustic phonon wave 
vector \( q \) should be well defined, that is, \( q \sim 4 \pi/\lambda_{\text{pump}} \) 
in the backscattering geometry. The displasive mechanism 5 also 
suggests a well-defined oscillation frequency. In both mod-
els, the oscillation frequency depends on \( \lambda_{\text{pump}} \) and not on 
\( \lambda_{\text{probe}} \) or \( \theta \) as experimentally observed. However, for the 
case of a propagating strain pulse model, the oscillation pe-
riod \( \tau_p \) is given by 

\[ \tau_p \sim (\lambda/2v_s) \sqrt{\eta - \sin^2 \theta} \]  

Here \( v_s \) is the sound velocity and \( n \) the refractive index of the material. 
A numerical calculation based on the propagating strain model 
using available refractive index data1 follows the measured 
oscillation period for several probe wavelengths very well 
[Fig. 1(b)]. Furthermore, the calculated dependence of \( \tau_p \) on 
\( \theta \) (using the aforementioned equation) provides an excellent 
fit to the experimental data [see Fig. 1(c)], giving further 
evidence that the periodic oscillations in \( \Delta R/R \) originate 
from a propagating strain field.

According to the propagating strain model, 17 the change 
in the reflectance has the following form:

\[ \Delta R(t) - \Delta R_0 \cos \left( \frac{4 \pi n v_s t}{\lambda} \cos \theta - \phi \right) e^{-t/\tau_d} \]  

where \( \Delta R_0 \) is the change in the amplitude of the oscillation, 
\( \lambda \) is the wavelength of the probe beam, \( n \) is the refractive index 
of the material, \( v_s \) is the sound velocity, \( \phi \) is the phase of the 
oscillation, and \( \tau_d \) is the dephasing time.

Figure 1(d) shows the periodic oscillations of \( \Delta R/R \) at 
\( \lambda_{\text{probe}} \approx 800 \text{ nm} \) for several temperatures. From fits to this 
data, \( \tau_p = (\lambda/2v_s) \right) 1/\sqrt{\eta - \sin^2 \theta} \), and \( \phi \) are extracted and plotted in 
Figs. 2(a), 2(b), and 3, respectively. \( \tau_p \) decreases by more than 10% 
on increasing the temperature from 30 to 220 K, while \( \tau_d \) decreases 
by a factor of 4. In addition to the changes in \( \tau_p \) and \( \tau_d \), a strong change in \( \phi \) (Fig. 3) is 
observed. Due to proximity of the probe wavelength to the \( d-d \) 
optical transition peak at 1.7 eV, where the complex refrac-
tive index \( n + ik \) varies strongly with temperature, we ex-

\[ \tau_d \sim \frac{\lambda}{2v_s} \frac{1}{\sqrt{\eta - \sin^2 \theta}} \]  

Errors are bigger than 10% upon increasing the temperature from 30 to 220 K, 
while \( \tau_d \) decreases by a factor of 4. In addition to the 
changes in \( \tau_p \) and \( \tau_d \), a strong change in \( \phi \) (Fig. 3) is 
observed. Due to proximity of the probe wavelength to the \( d-d \) 
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\[ \phi \sim \frac{\lambda}{2v_s} \frac{1}{\sqrt{\eta - \sin^2 \theta}} \]  

FIG. 1. Oscillations in \( \Delta R/R \) with (a) Pump at 800 and 400 nm with probe 
at 800 nm. (b) Probe wavelength dependence of oscillation period. Line is a 
numerical calculation based on propagating strain model. Errors are bigger 
for 740 and 700 nm due to rapid dephasing. (c) Probe incident angle depend-
dence. Solid circles are experimental data and the line is a fit with \( n = 2.5 \) 
and a sound velocity of 7640 m/s. Experiments (a)–(c) were done at room 
temperature. (d) Oscillations at various temperatures. For the data in (c) and 
(d) the pump was at 400 nm and probe at 800 nm.

FIG. 2. (a) Oscillation period vs temperature. The estimated sound velocity, 
as determined from the oscillation period and published value of \( n(T) \), is 
pictured in the inset. (b) Experimental dephasing time vs temperature (solid 
circles) and the calculated value from the probe absorption depth and sound 
velocity (open circles). (Pump at 400 nm, probe at 800 nm.)

FIG. 3. Phase shift as a function of temperature for probe 800 and 740 nm, 
pumped at 400 nm. The phase extracted from the experimental data is plot-
ted in solid circles (rectangles) and the calculation result, as open circles 
(rectangles) for probe 800 (740 nm). \( \phi_{\text{abs}} \) is plotted as triangles. \( \phi_0 \) was set 
equal to zero. The dispersion of \( \partial n/\partial T(\partial k/\partial T) \) is plotted as circles (rect-
angles) for probe wavelength 800 (740 nm) is solid (open) symbols in the 
inset.
pect measurable changes in $\tau_p$ and $\tau_d$, as observed. The sound velocity is not well known for LuMnO$_3$, so that a numerical estimate of the oscillation period ($\tau_p \sim \lambda/2nv_s$) is not possible. However, since the temperature dependence of refractive index is known, the oscillation frequency provides an easy method for measuring the sound velocity as a function of temperature. The result is shown in the inset of Fig. 2(a).

The dephasing time, shown in Fig. 2(b), also displays a strong dependence on temperature. The damping of the oscillatory signal can arise from two factors in the propagating strain model: (a) absorption of the probe (since the strain pulse propagates into the crystal, a finite penetration depth of probe leads to dephasing and (b) due to phonon decay ($\tau_{\text{decay}}$). We can write $1/\tau_d = 1/\tau_{\text{abs}} + 1/\tau_{\text{decay}}$, where $\tau_{\text{abs}} = (\lambda/4\pi v_s)k/k$ ($k$ is the extinction coefficient at $\lambda_{\text{probe}}$). A numerical estimate of $\tau_{\text{abs}}$ is obtained using the experimentally determined sound velocity [Fig. 2(a)] and extinction coefficient. As Fig. 2(b) shows, the numerically determined $\tau_{\text{abs}}$ agrees quite well with the experimental value of $\tau_d$. This suggests that dephasing is predominantly from the finite absorption depth of the probe rather than the decay time of acoustic phonons, and implies that $\tau_{\text{decay}} \gg \tau_d$.

In addition, a large change in phase $\phi$ has been observed, with a steep change near $T_N$, as shown in Fig. 3. In the propagating strain field model, $\phi$ arises from two factors: (i) the refractive index and extinction coefficient and (ii) their derivative with respect to strain $\eta_{33}$:

$$\phi = \phi_{nk} + \phi_{\text{strain}} + \phi_o,$$

$$\phi_{nk} = \tan^{-1} \left( \frac{k(n^2+k^2+1)}{n(n^2+k^2-1)} \right),$$

$$\phi_{\text{strain}} = -\tan^{-1} \left( \frac{\partial k}{\partial n} \right).$$

Here, $\phi_o$ is a temperature-independent constant Both $n$ and $k$ vary strongly with temperature since the probe energy is close to the $d-d$ transition energy $E_{d-d}$, which is strongly temperature dependent. As shown in Fig. 3, the change of $\phi_{nk}$ with temperature is small and is of opposite sign and has a minor effect on the overall $T$ dependence of $\phi$. Therefore, $\phi_{\text{strain}}$ should be responsible for the observed temperature-dependent phase shift. Since $\lambda_{\text{probe}}$ is close to the $d-d$ optical transition, we can assume that $\partial n, k/\partial \eta_{33}$ arises from the change of the $d-d$ transition energy. The temperature dependence can be directly described based on the temperature dependent $d-d$ transition energy as follows:

$$\frac{\partial n, k(T)}{\partial \eta_{33}} = \frac{\partial n, k(T)}{\partial E_{d-d}} \frac{\partial E_{d-d}}{\partial \eta_{33}} = \frac{\partial n, k(T)}{\partial T} \frac{\partial E_{d-d}(T)}{\partial \eta_{33}}.$$

In estimating $\phi_{\text{strain}}$, only $\partial n/\partial T$ and $\partial n/\partial T$ are needed, and they are plotted in the inset of Fig. 3 for $\lambda_{\text{probe}}$ at 800 and 740 nm. The estimated phases calculated from the $n$ and $k$ data (plotted in Fig. 3 with open circles and rectangles, respectively) agree with experimental result, which proves that strain term is mainly responsible for the observed phase change. $\partial n, k/\partial T$ depends strongly on the probe wavelength as shown in the inset and results in the phase difference between probing at 700 and 800 nm. However, at both wavelengths, there is a steep phase change in the vicinity of $T_N$, which reflects the fact that $n$ and $k$ change rapidly with temperature near $T_N$. The steep phase change in the vicinity of $T_N$ is consistent with the observed shift of the $d-d$ transition, which has been attributed to the coupling to the underlying magnetic order.

In conclusion, we have observed coherent acoustic phonons in LuMnO$_3$. The dependence of the oscillation frequency on the probe wavelength and the incident angle, and the temperature dependence of the oscillation frequency, dephasing time, and phase can be consistently explained by a propagating strain pulse model. It is found that the dephasing mechanism is due mainly absorption depth of the probe and that the temperature dependent phase of the oscillatory signal arises from the dispersion of $n$ and $k$ near the $d-d$ optical transition, which is coupled to the antiferromagnetic ordering.

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