Review Article

Understanding Multiferroic Hexagonal Manganites by Static and Ultrafast Optical Spectroscopy

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Multiferroic hexagonal manganites ReMnO₃ studied by optics are reviewed. Their electronic structures were revealed by static linear and nonlinear spectra. Two transitions located at ~1.7 eV and ~2.3 eV have been observed and attributed to the interband transitions from the lower-lying Mn³⁺dₓᵧ/dₓ²−ᵧ² and dₓzy/dᵧzx states to the Mn³⁺dᵧ²−z² state, respectively. These so-called d-d transitions exhibit a blueshift as decreasing temperatures and an extra blueshift near T_N. This dramatic change indicates that the magnetic ordering seriously influences the electronic structure. On the other hand, the ultrafast optical pump-probe spectroscopy has provided the important information on spin-charge coupling and spin-lattice coupling. Because of the strongly correlation between electronic structure and magnetic ordering, the amplitude of the initial rising component in ∆R/R shows striking changes at the vicinity of T_N. Moreover, the coherent optical and acoustic phonons were observed on optical pump-probe spectroscopy. Both the amplitude and dephasing time of coherent phonons also exhibit significant changes at T_N, which provide the evidence for spin-lattice interaction in these intriguing materials.

1. Introduction

Multiferroic materials [1–4] with the coexistence of various ferroic order (ferromagnetic, ferroelectric, or ferroelastic) have attracted great attention in condensed matter research due to their great potential for applications in the fields of oxide electronics, spintronics, and even the green energy devices for reducing the power consumption. With multiferroic oxides (in single phase), the coupling interaction among various order parameters causes the so-called magnetoelectric effect [5–10]. In this, a polarization can be induced by applying a magnetic field or a magnetization can be induced by applying an electric field. Although the properties of electricity and magnetism were combined into one common discipline by the Maxwell equations, the electric and magnetic orderings in solid-state materials are always considered separately. This is because that the electric charges of electrons and ions are responsible for the charge effects, whereas the electron spins govern the magnetic properties.

Prellier et al. [11] classified the characteristics of multiferroic materials into three categories. The first is Bi-based compounds, such as BiMnO₃ and BiFeO₃. The second is perovskites and related ReMnO₃ compounds (Re = Y, Ho, Er, Tm, Yb, and Lu). The third is ReMn₂O₅ (Re is rare earth element). Additionally, Cheong and Mostovoy [12] summarized the classification of ferroelectrics into “proper” and “improper” according to their mechanisms of inversion symmetry breaking. In proper ferroelectrics, the main driving force toward the polar state was associated with the electronic pairing. On the other hand, the induced polarization in improper ferroelectrics involves a more complex lattice distortion or other accidental orderings. For example, the hexagonal manganite ReMnO₃ compounds show a lattice distortion to enlarge their unit cell, which is the so-called geometric ferroelectricity [13–15].

The aim of this paper is to understand the multiferroic hexagonal manganites studied by some optical techniques. In Section 2, the overall features of manganites are introduced.
The structure of rare earth manganite is strongly depending on the size of rare earth and also temperature. The environment of Mn ions significantly affects its electronic structure which was investigated by static linear and nonlinear spectra in Section 3. Section 4 is the main part of this paper. The ultrafast spectroscopies demonstrate the interaction between electron, phonon, and spin systems on multiferroic hexagonal manganites. Finally, the summary and future outlook will be given in Section 5.

2. The Characteristics of Multiferroic Manganese ReMnO₃

Recently, multiferroic rare earth manganites (ReMnO₃) have attracted a great deal of attention due to their manifestations of intriguing and significant couplings between the magnetic and electric order parameters. Generally, ReMnO₃ has two kinds of multiferroic structures, that is, hexagonal and orthorhombic. The rare earth (Re³⁺) ionic size shrinks from 1.11 Å to 0.94 Å with decreasing the atomic number and reducing the electrons residing in the 4f orbit, called the lanthanum contraction effect. The rare earth ions (Re³⁺) have closely chemical properties because the same electronic configurations of 5s²⁵p⁶ for outermost electrons. The coexistence of ferroic orders in ReMnO₃ with hexagonal (smaller ionic radius of rare earth Re = Sc, Y, and from Ho to Lu) or orthorhombic (larger ionic radius of rare earth Re = La to Dy) (shown in Figure 1) structure yields complex physics in the intimate interactions among charge, orbital, lattice, and spin degrees of freedom. It also has fascinating physical properties which might lead to promising applications. The orthorhombic structure with a Pnma space group forms the stable crystal structure of ReMnO₃ perovskite oxides with Re = La to Dy, which belongs to the magnetic ferroelectrics induced by magnetic ordering [8, 16]. Furthermore, another family of compounds with smaller ionic size (for Re = Y, Ho, Er, Yb, Lu, etc.) forms the stable hexagonal structure with P6₃cm space group. The critical point of the structure transition is located near YMnO₃ (Y³⁺ = 1.06 Å) and HoMnO₃ (Ho³⁺ = 1.05 Å). Consequently, the crystal structures of these two families have been transformed from hexagonal to orthorhombic (or vice versa) by many experimental techniques, for example, high-temperature and high-pressure processes [17, 18], chemical solution deposition (CSD) [19], the metal-organic chemical vapor deposition (MOCVD) [20], molecular beam epitaxy (MBE) [21], sputtering [22], and pulsed laser deposition (PLD) [16, 23].

In the following, we are going to focus on recent studies on the multiferroic hexagonal manganites (ReMnO₃, Re = rare earth) which have properties similar to various rare-earth elements, both electric transport or magnetic behaviors. For example, the hexagonal HoMnO₃ has ferroelectric ordering at Curie temperature T_C = 875 K, the antiferromagnetic (AFM) Mn³⁺ ordering at Neel temperature T_N = 76 K, and the magnetic Ho³⁺ ordering at T_Ho = 4.6 K, in which the magnetically active ions are the high spin Mn³⁺ (3d⁵, S = 2) and Ho³⁺ (4f⁰) [5, 14, 33, 40–45]. The ferroelectricity in magnetoelectric ReMnO₃ is caused by a buckling of the layered MnO₂ polyhedral and is accompanied by displacements of the Re ions, which lead to a net electric polarization. In 2004, through X-ray diffraction and first principle density functional calculations, Van Aken et al. [14] demonstrated the previous scenario in the hexagonal manganite YMnO₃, as shown in Figure 2 which presents the “geometric” generation of polarization and describes the tilting of a rigid MnO₂ block with a magnetic Mn atom at the center. The magnetic structure has been studied by various experimental methods, such as neutron diffraction [45, 46] or second harmonic generation (SHG) [33, 47]. In
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3. Electronic Structure Revealed by Optical Spectroscopy

To understand the extensive physical properties in multiferroic ReMnO₃ materials, it is crucial to realize the electronic band structure. With respect to the crystal structure of hexagonal ReMnO₃ manganites with MnO₂ bipyramids, in contrast with the MnO₆ octahedron of orthorhombic structure which split to $t_{2g}$ and $e_{g}$, the crystal field symmetry leads the quintet d levels of Mn$^{3+}$ ion splits into two low lying doublets of $e_{2g}$ and $e_{1g}$ ($d_{xz}/d_{yz}$ and $d_{xy}/d_{z^2}−r^2$) states and one singlet $a_{1g}$ ($d_{3z^2}−r^2$) state. In general, optical spectroscopy is one of the powerful tools for investigating the electronic band structure in materials. Therefore, this structural difference between the hexagonal and orthorhombic phases could be disclosed by the optical spectra [60, 61].

3.1. Linear Optical Absorption Spectra. The first optical measurements in hexagonal YMnO₃ were performed by Kri-tayakiran et al. in 1969 [62], who observed that a near infrared absorption edge moves to higher energy with lowering temperature. For the case of hexagonal ScMnO₃ and ErMnO₃, the spectra of the rare earth ions of Re=Lu, Gd, Tb, Dy, and Ho, and the overall features in the spectra are similar to previous results. The most surprising part of those results is that the temperature-dependent absorption peak at ~1.7 eV shows an unexpectedly large blueshift near $T_N$ among the rare-earth ions of Re=Lu, Gd, Tb, Dy, and Ho, as shown in Figure 4(a).

The assignment of the optical absorption peak at ~1.7 eV has also been an issue. One interpretation is that it comes from the charge transfer transition from the O 2p to the Mn 3d states [30, 63, 65, 66]. The photoemission spectroscopy (PES) study proposed that the O 2p is the highest occupied state, while the Mn $d_{3z^2}−r^2$ state is mostly unoccupied. Other occupied Mn 3d states ($d_{xz}/d_{yz}$, and $d_{xy}/d_{z^2}−r^2$) lie deep below $E_F$ [65]. The result of the first-principle electronic structure calculations also suggested that the top of the valence band is mainly determined by the O 2p states, and the lowest unoccupied band is formed by the $d_{3z^2}−r^2$ of Mn [30, 66]. The other interpretation, which is also an extensively convincing explanation, is that it comes from on-site d-d transition between the Mn 3d levels [31, 34, 64, 67]. The transition was attributed to the d-d transition between occupied $e_{2g}$ and $e_{1g}$ ($d_{xz}/d_{yz}$, and $d_{xy}/d_{z^2}−r^2$) orbitals and the unoccupied $a_{1g}$ ($d_{3z^2}−r^2$) orbit, as shown in Figure 4(b). Because of the selection rule, transitions between d orbitals are forbidden. However, the selection rule is relaxed through the strong hybridization between the O 2p bands and transition metal d bands, which was observed in the hexagonal phase but not in the orthorhombic phase [60]. Furthermore, the strong peak at ~5 eV is attributed to the charge transition from the hybridized O 2p level to the Mn $d_{3z^2}−r^2$ level.

The other feature of the near infrared absorption peak is that it shows the blueshift as decreasing temperatures accompanying the dramatic changes near $T_N$, which indicates...
Figure 3: Electronic conductivity of LuMnO$_3$ at 300 K (dashed line) and 10 K (solid line). Inset: temperature-dependent peak position (open squares) and spectral weight (solid circles) of the absorption peak around 1.7 eV [31]. Reprinted figure with permission from Souchkov et al. [31]. Copyright (2003) by the American Physical Society.

Figure 4: (a) Upper panel: temperature dependence of the peak positions normalized to the peak position at $T_N$ as a function of the normalized temperature $T_{Nn} = T/T_N$. Lower panel: absolute value of normalized peak position differentiated to normalized temperature [32]. Reprinted figure with permission from Choi et al. [32]. Copyright (2008) by the American Physical Society. (b) Schematic diagram of the d-d transition in ReMnO$_3$. The red arrows indicate electrons reside in the d orbitals, and the gray arrow indicates lowering of $e_{2g}$ band caused by the temperature reduction.
the effective coupling between the electronic structure and the magnetic ordering. Souchkov et al. [31] attributed this temperature-dependent blueshift to the effects of exchange interactions between the Mn$^{3+}$ ions. The superexchange between Mn$^{3+}$ neighbors leads to lower d$_{xy}$/d$_{z^2}$ levels, whereas the d$_{xy}$ level is rarely affected (see Figure 4(b)). Moreover, together with the temperature-dependent and magnetic-dependent results [32] further implies that the magnetic ordering seriously influences the electronic structure.

3.2. Second Harmonic Generation Spectra. From the linear absorption spectra, the strong absorption caused by the d-d transition from e$_{2g}$ to a$_{1g}$ was clearly observed in hexagonal manganites. But the transition from e$_{1g}$ to a$_{1g}$ is another question. Recently, the second harmonic generation (SHG) was successfully used to explore the hidden localized d-d transitions, even those embedded in the much stronger absorption peaks [68]. The nonlinear polarization induced by optical waves is given by

$$\mathbf{P}_i(2\omega) = \varepsilon_0 \left( \chi^{(i)}_{ijk} + \chi^{(c)}_{ijk} \right) \mathbf{E}_j(\omega) \mathbf{E}_k(\omega),$$

where $\mathbf{P}_i(2\omega)$ is the nonlinear polarization induced in a medium. $\mathbf{E}_j(\omega)$ and $\mathbf{E}_k(\omega)$ are the electric field components of the fundamental light. $\chi^{(i)}_{ijk}$ and $\chi^{(c)}_{ijk}$ are the second-order nonlinear susceptibility tensor which are uniquely defined by the crystalline and magnetic structure of the crystal, respectively. The subscripts i, j, and k correspond to the Cartesian coordinate axes x, y, and z. i is the direction of the nonlinear polarization generated; j and k are the directions of applied optical field.

There are two types of optical SHG in multiferroic hexagonal manganites. One is caused by the noncentrosymmetric ferroelectric ordering of charges and the nonlinear susceptibility is time invariant (i-type). The other is due to the centrosymmetric antiferromagnetic ordering of spins and the susceptibility is time noninvariant (c-type) [34]. Table 1 lists the allowed susceptibility tensor components in i-type and c-type. Thus, the SHG contribution from ferroelectric and antiferromagnetic can be distinguished easily. Figure 5 summarizes the magnetic symmetries of all the hexagonal ReMnO$_3$ compounds as derived from the SHG experiments [33].

The polarization $\mathbf{P}^{FE}(2\omega)$ with the space group P6$_3$cm below the Curie temperature $T_C$ is

$$\mathbf{P}^{FE}_x(2\omega) = 2\varepsilon_0 \chi^{(0)}_{xxx} \mathbf{E}_x(\omega) \mathbf{E}_x(\omega),$$

$$\mathbf{P}^{FE}_y(2\omega) = 2\varepsilon_0 \chi^{(0)}_{xxy} \mathbf{E}_y(\omega) \mathbf{E}_y(\omega),$$

$$\mathbf{P}^{FE}_z(2\omega) = \varepsilon_0 \chi^{(0)}_{zzz} \mathbf{E}_z(\omega) + \varepsilon_0 \chi^{(0)}_{xyz} \mathbf{E}_y(\omega).$$

The contribution from antiferromagnetic $\mathbf{P}^{AFM}(2\omega)$ below $T_N$ for the space group P6$_3$cm (e.g., YMnO$_3$ [68, 69]) is

$$\mathbf{P}^{AFM}_x(2\omega) = 2\varepsilon_0 \chi^{(c)}_{xxy} \mathbf{E}_x(\omega) \mathbf{E}_y(\omega),$$

$$\mathbf{P}^{AFM}_y(2\omega) = \varepsilon_0 \chi^{(c)}_{yyy} \left[ \mathbf{E}_y^2(\omega) + \mathbf{E}_y^2(\omega) \right],$$

$$\mathbf{P}^{AFM}_z(2\omega) = 0.$$
4. Ultrafast Pump-Probe Spectroscopy

Ultrafast optical pump-probe spectroscopy has proven to be a powerful tool to investigate the dynamics of electron-electron interaction, electron-phonon interaction, and electron-spin interaction in various materials (see, e.g., [70–72]). To understand the underlying mechanisms in strongly correlated materials, the interactions between these order parameters should be derived first. Because of the different characteristic time scales and characteristic behavior for various degrees of freedom existing in these complex materials, ultrafast spectroscopy can determine the coupling between each order of parameters.

As shown in Figure 7, the general idea of the pump–probe technique is that changes of a sample induced by a pump pulse are obtained by detecting the change in the reflectivity (ΔR) or transmissivity (ΔT) of probe pulses as a function of probe delay time. The femtosecond time evolutions are derived by delaying the relative arrival time between the pump and probe pulses using a mechanical delay line. The fluence of a probe pulse is usually much weaker than that of a pump pulse in order to avoid second excitation in the samples. The polarizations of pump and probe pulses are set perpendicular to avoid interference between pump and probe beams [73].

Generally, this pump–probe spectroscopy composes two kinds of signals of the decay background and the oscillation, which relates to the relaxation of carriers and the dynamics of phonons or spins, respectively. By the Fourier transform, the frequency of phonon modes can be doubly obtained from the oscillation signals in pump-probe spectroscopy. Moreover, the phonon dynamics, that is, the time-evolution of oscillation signals, can be revealed by short-time Fourier transform (STFT), which cannot be reached by common Raman spectroscopy. Thus, the pump-probe spectroscopy is a powerful tool to provide the information in time- and frequency-domain simultaneously.

4.1. Spin-Charge Coupling. Since the magnetic ordering and the electronic structure of manganites are strongly correlated, as found in temperature-dependent absorption spectra, there is a strong coupling between charge and spin, which can be revealed by the time-resolved femtosecond spectroscopy.
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Figure 7: (a) Schematic diagram of pump-probe technique. Time delay ($\Delta t$) between pump and probe pulses can be controlled by a mechanical delay line. (b) The fundamental principle of pump-probe experiments. Time varying refractive index $n(t)$ changes of the sample induced by pump pulses were observed by detecting the intensity variations of probe pulses.

4.2. Spin-Lattice Coupling. Optically induced lattice vibration can be observed through optical pump-probe spectroscopy through a periodic oscillation. This periodic oscillation in reflectivity (or transmissivity), so-called coherent acoustic phonons, is caused by interference between the reflected probe beams from sample surface and the wave front of the propagating strain pulse generated upon the pump pulse [75, 76]. On the other hand, vibration with frequencies corresponding to optical phonon modes in various materials has been observed by pump-probe spectroscopy. A number of mechanisms have been proposed to explain these oscillations, for example, the displacive excitation of coherent phonons (DECP) [77] and the impulsive stimulated Raman scattering (ISRS) [78, 79]. The simplest idea is that a pump pulse creates a standing wave which was generated by the coherent ionic motion. Then a following probe pulse senses the changes of refractive index which is modulated by the standing wave. In general, the reflectivity (or transmissivity) oscillation observed in pump-probe spectroscopy always corresponds to the optical phonon modes observed in Raman spectroscopy. In conclusion, the measurements of coherent acoustic or optical phonons dynamics at various temperatures are useful to study the spin-lattice coupling in multiferroic materials.

4.2.1. Coherent Optical Phonons. Figure 9 shows the reflectivity oscillation of $\sim 3.6$ THz ($\sim 120$ cm$^{-1}$) in LuMnO$_3$ [36, 37]. According to Raman studies, this vibration mode can be attributed to optical phonon of $A_1$ symmetry [80–82]. This fully symmetric mode corresponds to the LuI and Lu2 atomic motions in opposite directions along the c-axis, as depicted in Figure 9(d) [36]. In temperature-dependent measurements, the optical phonon almost disappears below $T_N$, as shown in Figures 9(e) and 9(f) [37]. Additionally, the structural change from highly symmetry space group $P6_3/mmc$ to the tilted and distorted $P6_3/cm$ ferroelectric structure [14] in hexagonal manganites (see Figure 1) takes place at the Curie temperature ($T_C$), which is much higher than $T_N$. Since there is no structural transition near $T_N$, the atomic motions of the optical phonon mode would be affected by the appearance of magnetic ordering. In other words, the disappearance of optical phonon mode might be attributed to the magnetoelastic coupling. In temperature-dependent Raman studies, the lowest frequency $A_1$ mode also shows anomaly at $T_N$ in YMnO$_3$ [82], ErMnO$_3$ [83], and LuMnO$_3$ [80, 82] which support close relation between phonon and spin systems.

4.2.2. Coherent Acoustic Phonons. Coherent acoustic phonons have been observed in many kinds of hexagonal
manganites such as LuMnO$_3$ [37, 84], YMnO$_3$ [39], and HoMnO$_3$ [38]. The damped oscillation behavior in reflectivity changes with time delay $t$ could be described as follows [76]:

$$\frac{\Delta R}{R} \propto \left( \frac{\Delta R}{R} \right)_0 \cos \left( \frac{4\pi n v_s t}{\lambda} - \phi \right) e^{-\left(\nu_s/\xi\right)t},$$

where $\lambda$ is the wavelength of the probe pulses, $n$ is the refraction index of samples without strain, $v_s$ is the strained layer propagating sound speed, and $\xi$ is the penetration depth of probe pulses. The frequency of the oscillation is given as $\omega = 4\pi n v_s/\lambda$ and the dephasing time is $\xi/v_s$.

According to (4), the dephasing time is proportional to the penetration depth of probe pulses $\xi$ and the inverse sound velocity $1/v_s$. However, the skin depth is much shorter than the propagating length of the strain pulse. Therefore, the dephasing time is dominated by the finite penetration depth $\xi$ of the probe [84]. The dephasing time of acoustic phonons shows strong temperature dependence (Figure 10), and the anomalous increase of the dephasing time near $T_N$ might be because of the photon energy being close to the edge of d-d transition. In other words, the penetration depth increases and the absorption of probe photons for the d-d

**Figure 8:** (a) Normalized amplitude of $\Delta R/R$ as a function of temperature at various wavelengths. The insets illustrate splitting of the Mn$^{3+}$ energy levels in the local environment MnO$_5$ for photon energy above and below $E_{dd}$ ($T_1 > T_2$). (b) Energy gap $E_{dd}$ as a function of $T_0$. $E_{dd}$ is estimated from the wavelengths in (a). The dashed line emphasizes linear behavior in the high-temperature range. (c) The slope of temperature-dependent normalized amplitude of $\Delta R/R$ in (a) (gray thick lines) as a function of $T_0$ at various wavelengths. The dashed line emphasizes behavior of the slope [35]. Reprinted figure with permission from Shih et al. [35]. Copyright (2009) by the American Physical Society.
transition decreases (due to the blueshift of $E_{dd}$ as mentioned in Section 3.1) as the temperature decreases.

The amplitude and period of the oscillation component in $\Delta R/R$ show strong temperature dependence as shown in Figure II. Both of these parameters are clearly anomalous near the magnetic ordering temperature $T_N$. The amplitude of the oscillation component in $\Delta R/R$ gradually increases with decreasing temperature and reaches the maximum near a characteristic temperature ($\sim 190$ K for YMnO$_3$ [39] and $\sim 200$ K for LuMnO$_3$ [37]). Then it decreases when the temperature approaches $T_N$, as shown in Figure II(a). This may imply the appearance of AFM short-range ordering, as mentioned in [35]. On the other hand, the period of the oscillation component in $\Delta R/R$ also slightly shrinks with decreasing temperature. Surprisingly, it dramatically shrinks around $T_N$ as shown in Figure II(b). This strongly indicates the close correlation between AFM ordering and the propagation of thermal stress along $c$-axis, which is consistent with the results in heat capacity measurements [13, 85]. In addition, the ferroelectric polarization along the $c$-axis caused by polyhedron tilting of MnO$_5$ and distortion of the rare-earth ions [14] is well known. Thus, the propagation of a strain pulse with the modulation of dielectric constant (or ferroelectric polarization) along $c$-axis is indeed affected by the appearance of AFM ordering. Neutron diffraction experiments also have demonstrated the extra displacement of the rare-earth and oxygen atoms along $c$-axis at $T_N$ [52]. Finally, these results in amplitude and period of the oscillation component in $\Delta R/R$ provide evidence for magnetoelastic coupling in these intriguing materials.

5. Summary and Outlook

In this paper, the recent developments on the electronic structures and ultrafast dynamics of hexagonal manganites have been reviewed. The electronic structure can be clearly revealed by the static linear optical absorption spectra and nonlinear second harmonic generation spectra. The temperature-dependent d-d transition energy exhibits an unexpected change near the spin ordering temperature $T_N$. This strongly indicates the coupling between electronic structure and antiferromagnetism in hexagonal manganites. Fortunately, the photon energy of the pulse laser used in pump-probe spectroscopy accidentally fits well the d-d transition (from $e_{2g}$ to $a_{1g}$) energy. Therefore, the pump-probe
mechanisms can reveal the ultrafast dynamics through the spin-charge coupling and spin-phonon coupling.

However, those ultrafast dynamic experiments only present the charge dynamics between $e_{2g}$ and $a_{1g}$. If the laser spectrum could cover the whole range of d-d transition, that is, containing the transition from $e_{1g}$ to $a_{1g}$ and $e_{2g}$ to $a_{1g}$, it could disclose all of the charge dynamics in these strongly magnetic influenced d orbitals. The optical parametric amplifier (OPA) is a suitable light source for this kind of study. Consequently, if all of the charge dynamics in the d orbitals could be completely revealed, it would shed light on the microscopic mechanism of the magnetoelectric coupling or magnetoelastic effect in this kind of strongly correlated material.

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