Exchange interaction effects on the optical properties of LuMnO$_3$

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We have measured the optical conductivity of single crystal LuMnO$_3$ from 10 to 45000 cm$^{-1}$ at temperatures between 4 and 300 K. A symmetry allowed on-site Mn $d$-$d$ transition near 1.7 eV is observed to blue shift ($\sim$0.1 eV) in the antiferromagnetic state due to Mn–Mn superexchange interactions. Similar anomalies are observed in the temperature dependence of the TO phonon frequencies which arise from spin-phonon interaction. We find that the known anomaly in temperature dependence of the quasi-static dielectric constant $\varepsilon_0$ below the $T_N \sim 90$ K is overwhelmingly dominated by the phonon contributions.

The colossal magnetoresistance compounds based on doped pseudo-cubic LaMnO$_3$ have excited much attention because of their interesting physical properties and potential applications. Another series of RMnO$_3$ materials (R=Ho,Er,Tm,Yb,Lu, or Y,Sc,In) have smaller radius $R^{3+}$ ions and crystallize in the hexagonal lattice. The hexagonal manganites are interesting as examples of multiferroics (or ferroelectromagnets) – they are both ferroelectric ($T_c$=900 K) and strongly frustrated antiferromagnets ($T_N$=90 K). The coupling between ferroelectric and magnetic order parameters provides the prospect of manipulating electrical properties through magnetic fields and vice versa which, in turn, gives these compounds potential for applications in electronics.

There have been several reports on the magnetic structure and aspects of the electromagnetic response in hexa-manganites. Of particular interest is the observation of a temperature anomaly of the static dielectric constant, $\varepsilon_0$, below $T_N$. In this letter, we present a systematic study of the linear optical response of LuMnO$_3$ which elucidates the origin of the $\varepsilon_0$ anomalies and the effects of the Mn–Mn exchange energy on the electrodynamics of this system. We show that the exchange interaction manifests itself in an antiferromagnetic resonance, spin-phonon coupling, and the temperature dependence of a 1.7 eV on-site Mn $d$-$d$ optical transition. The results give a comprehensive view of the magnetic and electronic structure of this interesting ferroelectric and strongly frustrated antiferromagnetic material.

The high-temperature paraelectric phase in the hexagonal manganites may be considered as layers of corner-sharing Mn$_5$O$_7$ triangular bipyramids connected by a layer of $R$-ions. In the ferroelectric phase, $R$-ions alternate their $c$-axis coordinates, producing a net electric moment of the unit cell, and the MnO$_5$ pyramids tilt away from the $c$-axis. The $d$-orbitals of the Mn$^{3+}$ ion in a triangular bipyramid of five O$^{2-}$ ions are split by the crystal field into three groups: $d_{x^2-y^2}$, $d_{xy}$, and $d_{z^2-r^2}$, in order of increasing energy. The latter orbital has the highest energy as the Mn-apical O bond lengths are shorter than in-plane distances. The in-plane $d_{xy}$ and $d_{z^2-r^2}$ orbitals are strongly hybridized with oxygen $p$ orbitals. In the ground state of the Mn$^{3+}$ ion four electrons occupy four lowest orbitals giving $<L>=0$ and $S=2$. Below $T_N$, spins are ordered antiferromagnetically in-plane and out-of-plane. The Néel temperature in hexa-manganites is 6–10 times smaller than the Weiss temperature which is due to the spin frustration in the triangular planar lattice and weak inter-plane exchange interaction.

Single crystals of LuMnO$_3$ were grown using the traveling floating zone method and characterized by magnetization, resistivity, and x-ray powder diffraction. The lattice constants as well as the observed macroscopic properties agree well with measurements reported in literature. Platelet samples were cleaved perpendicular to the $c$-axis. In our experiments, we studied a 25 $\mu$m thick $5 \times 1.5$ mm$^2$ sample and a $1.5 \times 2 \times 4$ mm$^2$ sample (for $c$-axis response). Transmittance and reflectance measurements were performed using a Fourier transform spectrometer in a frequency range from 10 to 45000 cm$^{-1}$ (1.2 meV to 5.6 eV). Temperature dependence from 4 to 300 K is achieved using liquid He in a continuous flow cryostat (sample in vacuum) with optical access windows.

The optical spectrum of LuMnO$_3$ is dominated by phonons in the 28–100 meV photon energy range and electronic transitions starting at $\sim$1.1 eV. The material...
is consistent with selection rules for the on-site Mn observed in the hexagonal phase but not ortho-YMnO$_3$. The fact that this feature is

![Figure 1: The electronic conductivity of LuMnO$_3$ at 300 K (dashed line) and 10 K (solid line). Inset: temperature dependence of the peak energy (open squares) of the 1.7 eV feature and its spectral weight (solid circles).](image)

strongly temperature dependent. The anomaly at $T_N$ indicates that at least part of the shift is associated with the magnetic phase transition. A spectral shift due to thermal expansion is also expected. However, the observed shift is larger than is typically observed in interband features in solids ($\sim 0.1$ eV). We attribute the magnetic part of the shift to the effects of the exchange interactions between the Mn ions. Level shifts of the Mn d-levels due to superexchange between Mn neighbors leads to a lowering of the $d_{z^2}$ levels in the antiferromagnetic state while the relatively isolated $d_{z^2}$ orbital is little affected. We believe that the shift in the resonance energy between 4 K and $T_N$ ($\sim 0.05$ eV) underestimates the exchange energy. This is partly because short range antiferromagnetic correlations in this frustrated magnetic system are expected and are observed to persist to higher temperatures $T_N$. Also, the absence of a shift in the 5 eV feature argues against such a large thermal shift in the 1.7 eV feature since they share the same final state. In addition, the extremely weak decrease in the oscillator strength of the 1.7 eV feature also argues against a strong thermal expansion effect since this optical transition, which is allowed only due to the hybridization with the O p states, is more sensitive to the lattice constant than are the level shifts. At present, however, we cannot separate the exchange effects from the effects of the thermal expansion on the optical transition energy. This will require a detailed analysis of the thermal effects. For completeness we note that magnetostriction can also produce level shifts due to the changes in the magnetic part of the shift to the effects of thermal expansion and can be safely neglected.

We can also estimate the exchange energy of the Mn spins from the Weiss temperature in the susceptibility.
From molecular field theory: $k_B \theta = z J_{NN} S(S + 1)/3$ where $\theta$ is the Weiss temperature, $z=6$ is the number of nearest neighbors. Therefore the exchange energy for the manganese ion is $E_{ex} \cong 3k_B \theta$. In the literature $\theta$ data for LuMnO$_3$ range between -519 K [12] and -887 K [11], so that $E_{ex}$ is in the range 140 to 240 meV, which is somewhat larger than our estimate from the optical shifts. As noted, however, this estimate ignored the additional shift expected above $T_N$ due to the effects of frustration. Also, these two estimations represent different manifestations of the exchange interaction. The Weiss temperature represents the ground state exchange energy between the ground and excited state of the Mn$^{3+}$ ion. Therefore, the two estimates are in satisfactory agreement and our assignment of the magnetic shift of the 1.7 eV peak with temperature to the differences in exchange interaction in excited and ground optical states of a given Mn ion is reasonable.

The phonon part of the conductivity spectrum of LuMnO$_3$ is shown in Fig. 2 (a) and (c). Mode assignments can be made by analogy with the assignment in Y MnO$_3$ [2]. Panels (b) and (d) in Fig. 2 show the temperature dependence of the frequency shifts. The two low frequency vibrational modes in the $E \perp c$ polarization display the strongest absolute frequency shifts ($\Delta \omega_0$), relative frequency shifts ($\Delta \omega_0/\omega_0$), and inflection points at $T_N$. This observation suggests that these modes are coupled to the spin system. Measurements of the phonon spectrum in the $E||c$ polarization on a $ab$-plane sample show only a thermal shift of the phonons (Fig. 2c). The frequency shift of the spin-coupled phonon appears very similar to the temperature dependence of the 1.7 eV feature. This suggests that both are related to the same, nearest-neighbor spin correlation function: $< S_i \cdot S_j > (T)$. The phonon shifts are understood in terms of the phonon induced modulation of the exchange energy produced by the ion modal displacements. The change in exchange energy produces a corresponding change in the effective restoring force for the phonon. The resulting shift will be $\Delta \omega^2(T) = \Delta k/M$, where $\Delta k \sim < S_i \cdot S_j >$ is the exchange energy contribution to the force constant and $M$ is the reduced mass of the phonon mode. In addition to frequency shifts due to the exchange effects there will also be shifts due to the thermal expansion of the lattice. The exchange energy is dominated by superexchange between nearest neighbor Mn ions separated by oxygens. However, due to the complexity of the hybridized Mn d-states there are both ferromagnetic and antiferromagnetic contributions that differ for in- and out-of-plane neighbors.

The anomaly in temperature dependence of the static in-plane dielectric constant below the Néel temperature is considered to be one of the manifestations of coupling between magnetic and ferroelectric order parameters in the ferroelectromagnets [1]. On the other hand, $\epsilon_0$ is determined by all of the oscillators present in the optical response of the system. We have examined the contributions to the quasi-static dielectric constant of LuMnO$_3$. Three groups of oscillators contribute to $\epsilon_0$: ferroelectric domains, phonons, and electronic transitions. The contribution from the antiferromagnetic resonance, centered at 50 cm$^{-1}$ at 10 K, is negligible. The contributions from ferroelectric domains falls off with frequency becoming negligible at the MHz frequencies of the quasi static measurements and, even more so, at the far-infrared frequencies of our measurements. Figure 3 shows the temperature dependence of the real part of the dielectric constant of LuMnO$_3$. The top curve in panel (a) reproduces quasi-static data of Katsufuji et al. [11]. The bottom curve in panel (a) was calculated from the measured frequency shift of the first interference maximum in the transmittance spectrum centered at 53 cm$^{-1}$. The value of $\epsilon_1$ at this frequency is determined by all optical phonons and all electronic oscillators. Panel (b) contains $\epsilon_1$ determined from the interference fringes in the mid-infrared transparency region midway between the phonon and electronic absorption bands. The value of $\epsilon_1 \equiv \epsilon_\infty$ at this frequency is due to the electronic transitions. Panel (c) shows an estimation of the input to the dielectric constant from the 1.7 eV electronic peak using $\Delta \epsilon_1 = 2/\pi \int_{\epsilon_1}^{\infty} d\epsilon \epsilon_2(\omega)/\omega$. From the data of Fig. 3 we conclude that practically all of $\Delta \epsilon$ below $T_N$ comes from phonon hardening. Comparing panels (a) and (b), only $\sim 5\%$ of this change is due to the shift of the 1.7 eV electronic peak. We can also conclude from panels (b) and (c) that the temperature dependence of $\epsilon_\infty$ is almost
FIG. 3: Temperature dependence of the dielectric constant $\varepsilon_1$ of LuMnO$_3$. Top (a) and middle (b) panels represent $\varepsilon_1$ measured from the etalon interference effect. Panel (c) shows the contribution of the 1.7 eV peak to $\varepsilon_1$ determined from the optical sum rule. The lines are guides to the eye.

entirely due to the 1.7 eV feature.

The absence of a magnetic anomaly in phonons in the $E||c$ polarization is consistent with the observed anisotropy in the static dielectric constant $\Delta\varepsilon$. Toward developing an understanding of this anisotropy of the spin lattice coupling we note that there are important distinctions between the $E||c$ and $E \perp c$ polarizations in the exchange modulation for this layered system. In the case of $E||c$ polarization the relative displacement of the in-plane Mn and O ions is transverse to their bond and bond stretching occurs only with the apical oxygen, primarily affecting the Mn $z^2$ orbital which is empty. Whereas for $E$ in the $ab$-plane both transverse and bond stretching Mn-O displacements are induced and the occupied in-plane orbitals are involved. This observation suggests that the in-plane bond stretching displacements dominate the spin-phonon interaction effects. The role of dynamic effective charge transfer for the bond stretching modes in transition metal compounds for ferroelectricity and the electron-phonon interaction has been recently discussed (see, for example, [R]). We suggest that the observed anisotropy of the spin-phonon coupling and $\varepsilon_0$ might be a consequence of dynamic charge redistribution for in-plane vibrations of Mn ions, which modulate the in-plane partially covalent bonds, and the absence of the effective in-plane charge redistribution for the out-of-plane modes.

More generally the question of a coupling between the two order parameters of this material is interesting. Within the Landau theory of phase transitions there are symmetry allowed terms in the Landau free energy describing the coupling between the magnetic and ferroelectric order [H]. The experimental data on the quasi-static dielectric constant implies that this term is of the form $\delta F \sim L^2 P^2 (E_{ph}^2 + E_{el}^2)$, where $P$ and $L$ are, respectively, the ferroelectric and antiferromagnetic order parameters. Establishing this coupling and relating it to the microscopic physics is a key issue in the study of this class of materials.

In conclusion, we have observed a strong coupling of the antiferromagnetism in LuMnO$_3$ to a sharp low energy interband transition and to the infrared phonon spectrum. The optical feature has a large blue shift associated with the antiferromagnetism which is caused by the effects of the exchange interaction on the on-site Mn $d$-$d$ transition. A similar anomaly in the temperature dependence of the phonon frequencies is attributed to effects of spin-phonon coupling. These results demonstrate that optical spectroscopy is a powerful tool in the study of exchange interaction in the strongly frustrated magnetic system of the hexagonal manganites.

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