Exchange Interaction Effects on the Optical Properties of $\mathrm{LuMnO_3}$

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We have measured the optical conductivity of single crystal $\mathrm{LuMnO_3}$ from 10 to 45 000 $\mathrm{cm^{-1}}$ at temperatures between 4 and 300 K. A symmetry allowed on-site Mn *d-d* transition near 1.7 eV is observed to blueshift (~ 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 the temperature dependence of the quasistatic dielectric constant ϵ_0 below $T_N \sim 90$ K is overwhelmingly dominated by the phonon contributions.

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The colossal magnetoresistance compounds based on doped pseudocubic $\mathrm{LaMnO_3}$ have excited much attention because of their interesting physical properties and potential applications. Another series of $R\mathrm{MnO_3}$ 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) [1]—they are both ferroelectric ($T_c \sim 900$ K) and strongly frustrated antiferromagnets ($T_N \sim 90$ 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 [2–4] and aspects of the electromagnetic response in hexa-manganites [4–9]. Of particular interest is the observation of a temperature anomaly of the static dielectric constant ϵ_0 below T_N. In this Letter, we present a systematic study of the linear optical response of $\mathrm{LuMnO_3}$ which elucidates the origin of the ϵ_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 $\mathrm{MnO_5}$ 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 $\mathrm{MnO_5}$ pyramids tilt away from the c axis. The d orbitals of the $\mathrm{Mn^{3+}}$ ion in a triangular bipyramid of five $\mathrm{O^{2-}}$ ions are split by the crystal field into three groups: $d_{xz,yz}$, d_{xy,x^2-y^2}, and $d_{3z^2-r^2}$, 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,x^2-y^2} orbitals are strongly hybridized with in-plane oxygen p orbitals. In the ground state of the $\mathrm{Mn^{3+}}$ ion four electrons occupy four lowest orbitals giving $\langle L\rangle = 0$ and $S = 2$. Below T_N, spins are ordered antiferromagnetically in-plane [3,4]. 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 interplane exchange interaction.

Single crystals of $\mathrm{LuMnO_3}$ 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 μm thick 5×1.5 $\mathrm{mm^2}$ sample and a $1.5 \times 2 \times 4$ $\mathrm{mm^2}$ sample (for c-axis response). Transmittance and reflectance measurements were performed using a Fourier transform spectrometer in a frequency range from 10 to 45 000 $\mathrm{cm^{-1}}$ (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 $\mathrm{LuMnO_3}$ is dominated by phonons in the 28–100 meV photon energy range and electronic transitions starting at $\sim$1.1 eV. The material is transparent below 28 meV and between 0.1–1.2 eV.

Figure 1 shows the electronic part of the optical conductivity spectrum of $\mathrm{LuMnO_3}$ calculated by Kramers-Kronig relations from the reflectance spectrum measured at 10 and 300 K. The lowest electronic excitation centered

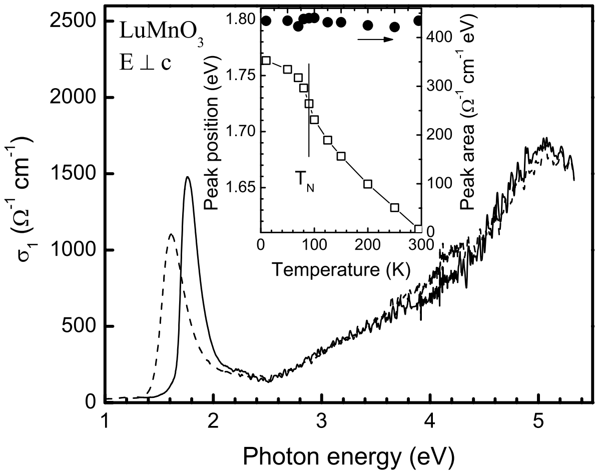

FIG. 1. The electronic conductivity of $\mathrm{LuMnO_3}$ at 300 K (dashed line) and 10 K (solid line). Inset: temperature dependence of the peak energy (open squares) of the 1.7 eV feature and its spectral weight (solid circles).

at ~1.7 eV is seen to be strongly temperature dependent. A similar effect has been reported for hexa-$\mathrm{YMnO_3}$ [5], whereas in ortho-$\mathrm{YMnO_3}$ this peak is not observed or is very weak [8]. From the inset in Fig. 1 it is seen that the resonance energy decreases monotonically with temperature having an inflection point at $T_N \sim 90$ K, while the integrated spectral intensity of this excitation is constant to within an experimental accuracy of about 2%. This feature is sitting near the foot of a large spectral feature which has a weak but sharp onset at 1.1 eV and is maximum near ~5 eV. The 1.1 to 5 eV conductivity band is independent of temperature to within our measurement accuracy.

We understand the electronic conductivity spectrum in terms of a broad band of charge transfer transitions from the hybridized oxygen p levels to the Mn $d_{3z^2-r^2}$ levels centered at ~5 eV and an on-site Mn d-d transition centered at 1.7 eV. The fact that this feature is observed in the hexagonal phase but not ortho-$\mathrm{YMnO_3}$ is consistent with selection rules for the on-site Mn d-d transitions in hexagonal and (near) cubic symmetry. Its interpretation as a charge transfer transition between Mn neighbors is ruled out because the spin dependence of the charge transfer matrix elements would lead to a strong temperature dependence of its oscillator strength which is not observed.

We have calculated the energies and spectral intensities of electronic transitions in the $\mathrm{MnO_5}$ complex in the framework of ligand-field theory. The electronic states are taken to be the Mn d orbitals coupled to the oxygen p_σ orbitals. Taking the energy of the $d_{x^2-y^2,xy}$ pair as zero, the energy of O p orbitals is $\Delta = -3$ eV, and the crystal field energy of the $d_{3z^2-r^2}$ orbital is $\Delta_{\mathrm{CF}} = 0.7$ eV. For the symmetric (paraelectric) structure, the hybridization is $t_1 = t_2 = 1.9$ eV for apical and $t_3 = t_4 = 1.7$ eV for in-plane oxygens. The allowed optical transitions for the $E \perp c$ polarization of light are $d_{(x^2-y^2)',(xy)'} \rightarrow d_{(3z^2-r^2)'}$ at 1.58 eV and from the two in-plane bonding O $p \rightarrow d_{(3z^2-r^2)'}$ at ~6.3 eV, where the prime denotes the corresponding d states as hybridized with the oxygen orbitals. The calculated spectral weights of both types of transition are a factor of 4 smaller than observed, but their ratio is correct. This discrepancy may be attributed to the neglect of the Mn p and s orbitals which can also couple to the O p states in the hexagonal symmetry. In the case of $E \parallel c$ polarization of incident light the optical matrix elements for the $d_{(x^2-y^2)',(xy)'} \rightarrow d_{(3z^2-r^2)'}$ transitions are zero as we find experimentally.

What is the origin of the ~0.15 eV shift of the 1.7 eV peak with temperature shown in Fig. 1? 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 (~ 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 $d_{x^2-y^2,xy}$ levels in the antiferromagnetic state, while the relatively isolated $d_{3z^2-r^2}$ orbital is little affected. We believe that the shift in the resonance energy between 4 K and T_N (~ 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 [10,11]. 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 lattice constant. However, these effects are much smaller than 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: $k_B\theta = zJ_{NN}S(S+1)/3$, where θ is the Weiss temperature and $z = 6$ is the number of nearest neighbors. Therefore, the exchange energy for the manganese ion is $E_{\mathrm{ex}} \cong 3k_B\theta$. In the literature θ data for $\mathrm{LuMnO_3}$ 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 manganese moments, while the optical shift represents the change in exchange energy of the Mn ion 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 Figs. 2(a) and 2(c). Mode assignments can be made by analogy with the assignment in $YMnO_3$ [7]. 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 $E \parallel c$ polarization on a ac-plane sample show only a thermal shift of the phonons [Fig. 2(d)]. 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: $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle(T)$.

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 $\Delta k \sim \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ 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, ϵ_0 is determined by all of the oscillators present in the optical response of the system. We have examined the contributions to the quasistatic dielectric constant of $LuMnO_3$. Three groups of oscillators contribute to ϵ_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 megahertz frequencies of the quasistatic 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 quasistatic 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 ϵ_1 at this frequency is determined by all optical phonons and all electronic oscillators. Panel (b) contains ϵ_1 determined from the interference fringes in the midinfrared transparency region midway between the phonon and electronic absorption bands. The value of $\epsilon_1 \equiv \epsilon_\infty$ at

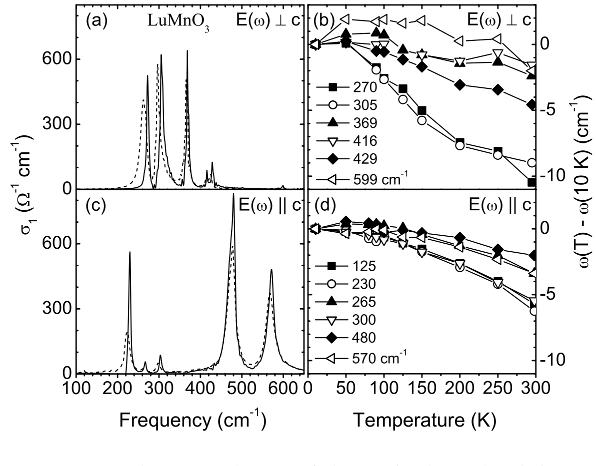

FIG. 2. (a) and (c): Real part of the optical conductivity σ_1 of $LuMnO_3$ in the phonon spectral range for 10 K (solid curves) and 300 K (dashed curves) for two polarizations of light; (b) and (d): temperature shifts of the phonon frequencies.

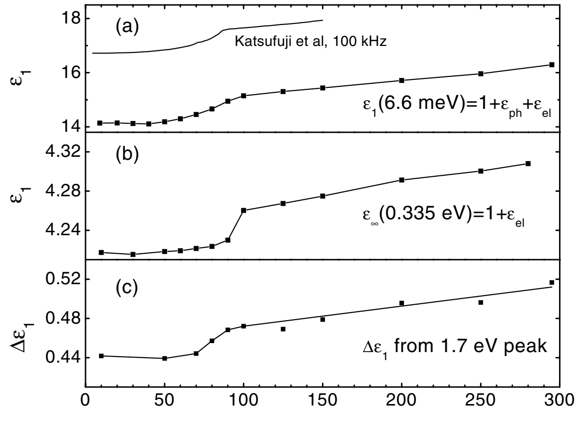

FIG. 3. Temperature dependence of the dielectric constant ϵ_1 of $LuMnO_3$. Top (a) and middle (b) panels represent ϵ_1 measured from the etalon interference effect. Panel (c) shows the contribution of the 1.7 eV peak to ϵ_1 determined from the optical sum rule. The lines are guides to the eye.

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 $\Delta\epsilon_1 = 2/\pi \int_{1\text{ eV}}^{2.5\text{ eV}} d\omega\epsilon_2(\omega)/\omega$. 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 ϵ_∞ is almost entirely due to the 1.7 eV feature.

The absence of a magnetic anomaly in phonons in the $E \parallel c$ polarization is consistent with the observed anisotropy in the static dielectric constant [11]. Toward developing an understanding of this anisotropy of the spin lattice coupling, we note that there are important distinctions between the $E \parallel c$ and $E \perp c$ polarizations in the exchange modulation for this layered system. In the case of $E \parallel c$ 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, [13]). We suggest that the observed anisotropy of the spin-phonon coupling and ϵ_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 [1]. The experimental data on the quasistatic dielectric constant implies that this term is of the form $\delta F \sim L^2P^2(E_x^2 + E_y^2)$, where P and L are, respectively, the ferroelectric and antiferromagnetic order parameters. Establishing this coupling and relating it to 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 blueshift 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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