Infrared studies of a La$_{0.67}$Ca$_{0.33}$MnO$_3$ single crystal: Optical magnetoconductivity in a half-metallic ferromagnet

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The infrared reflectivity of a La$_{0.67}$Ca$_{0.33}$MnO$_3$ single crystal is studied over a broad range of temperatures (78–340 K), magnetic fields (0–16 T), and wave numbers (20–9000 cm$^{-1}$). The optical conductivity gradually changes from a Drude-like behavior to a broad peak feature near 5000 cm$^{-1}$ in the ferromagnetic state below the Curie temperature $T_C = 307$ K. Various features of the optical conductivity bear striking resemblance to recent theoretical predictions based on the interplay between the double exchange interaction and the Jahn-Teller electron-phonon coupling. A large optical magnetoconductivity is observed near $T_C$.

The infrared reflectivity of a La$_{0.67}$Ca$_{0.33}$MnO$_3$ single crystal was grown by a floating zone method. X-ray diffraction confirms that the sample is single-phased with an orthorhombic structure close to cubic. The temperature-dependent magnetization of this La$_{0.67}$Ca$_{0.33}$MnO$_3$ single crystal reveals that the Curie temperature $T_C$ is at 307 K ($\pm 1$ K), and the resistivity $\rho(T)$ shows a monotonic decrease with decreasing temperature over the region investigated, with a significant change in the slope at $T_C$.

Near-normal incidence reflectivities were measured with a combination of a Fourier transform spectrometer, “Bruker” IFS 113v, and grating monochromator, to cover the frequency range from 20 to 25 000 cm$^{-1}$. The far-IR reflectivity spectra were studied in the Faraday geometry over 20–800 cm$^{-1}$ by using a “Bruker” IFS 113v spectrometer equipped with a superconducting magnet of field strength up to 18.5 T. The reflectivities were calibrated against a reference Au mirror in the far-IR region, and against a reference Al mirror at higher frequencies.

The reflectivity spectra of the La$_{0.67}$Ca$_{0.33}$MnO$_3$ single crystal for different temperatures from above $T_C$ down to 78 K and for wave numbers up to 9000 cm$^{-1}$ are shown in Fig. 1, with more details up to 800 cm$^{-1}$ given in the inset. The reflectivity spectra above $T_C$ reveal three distinct optical phonon features near 170, 350, and 580 cm$^{-1}$. These features are interpreted as the cubic perovskite vibration bands of the $F_{1u}$ symmetry. As the temperature decreases from 340 to
78 K, the reflectivity displays a gradual increase, consistent with the occurrence of a metallic FM phase at low temperatures. The optical phonon modes evident above 250 K become screened and eventually disappear in the metallic phase.

To obtain the optical conductivity through the Kramers-Kronig analysis, we used a Hagen-Rubens extrapolation for the low-frequency region. Extrapolation towards high frequencies was made by using the reflectivity data of La$_{1-x}$Sr$_x$MnO$_3$ from 25 000 to 80 000 cm$^{-1}$ because these data are nearly independent of the temperature and doping level. For energies higher than 80 000 cm$^{-1}$, an extrapolation using the $\omega^{-4}$ frequency dependence was used. The real part of the optical conductivity $\sigma(\omega)$ for different temperatures from above $T_C$ down to 78 K is shown in Fig. 2. The Drude approximation with a frequency-independent contribution from the transverse optical (TO) phonons and for the mid-IR bands. We find that at low temperatures ($T \leq 150$ K), the $\sigma(\omega)$ spectrum exhibits a dominant Drude-like contribution, yielding a plasma frequency $\omega_p=2.6 \times 10^4$ cm$^{-1}$, a scattering rate $\gamma=5.5 \times 10^3$ cm$^{-1}$, and a high-frequency dielectric constant $\varepsilon_\infty \approx 7.5$ at 78 K, as shown by the dashed line in Fig. 2. In the context of half-metallic ferromagnetism below $T_C$, these parameters provide an estimate for the majority carrier density per Mn, $n$, corrected by the effective mass, $m^*$, via the relation $nm^*/m^*=\omega_p^2/(4\pi N_{\text{Mn}}e^2) \approx 0.40-0.45$, where $N_{\text{Mn}}$ is the number of Mn atoms per unit volume. Assuming an effective carrier concentration $n=2/3$ which is comparable to the doping level, we obtain a reasonable effective band mass $m^* \approx 1.5-2m_e$.

With increasing temperature, we find that the spectral weight of the Drude component gradually decreases. At temperatures above 250 K, the spectral weight is appreciably transferred to the broad mid-IR band. As shown in Fig. 2, the optical conductivity at $T \geq 250$ K exhibits a broad peak on a continuum, extending from the mid-IR region to the lowest frequencies. Well above $T_C$, in the PM phase and may be treated as a contribution from the interband excitations. In the inset of Fig. 2, we show the temperature dependence of the total spectral weight of the Drude and mid-IR contributions derived from the Drude-Lorentz analysis, expressed in terms of the effective electron density per Mn site:

$$N_{\text{eff}} = \frac{2m_e}{\pi \varepsilon_\infty^2 N_{\text{Mn}}} \int [\sigma_{\text{Drude}}(\omega) + \sigma_{\text{mid-IR}}(\omega)] d\omega. \quad (1)$$

As shown in the inset of Fig. 2, $N_{\text{eff}}$ is not a conserved quantity: It decreases monotonically with increasing temperature in the FM state, and then exhibits a sharp drop at the Curie temperature.

The experimental observation of the frequency-dependent optical conductivity may be understood in terms of a theoretical model that incorporates both the DEX transport mechanism and an electron-photon coupling effect. In a dynamical mean-field approximation, it is assumed that the d electron in the $e_g$ orbital of the Mn$^{3+}$ ion is coupled to $3t_{2g}$ spins of Mn ions via the Hund’s rule exchange coupling, and to the classical oscillators of the lattice through the Jahn-Teller effect. It is found that $T_C$, $\sigma(\omega,T)$, and $\rho(T)$ are functions of an effective coupling parameter $\lambda$, defined as the ratio of the energy gain from localizing an electron at the Mn site to the electron kinetic energy, $t$. That is, $\lambda = E_{JT}/t$ and $E_{JT} = g^2/(2k)$, where $g$ is the electron-photon coupling strength, $k$ the force constant of the classical oscillators. Comparing our data with Ref. 9, we find that the effective coupling parameter $\lambda$ is comparable to unity, suggesting a moderate electron-photon coupling in La$_{0.67}$Ca$_{0.33}$MnO$_3$. The broad peak in the mid-IR optical conductivity can be attributed to transitions between the two $e_g$ orbitals of adjacent Mn sites, and is therefore comparable to the Jahn-Teller splitting. Comparing our optical conductivity data (which...
Neff cannot be entirely accounted for by the temperature dependence of the PM state, the latter involving an excitation energy of the level in the FM state to effectively interband excitations in spectral weight, from intraband excitations near the Fermi level. The CMR man- ganites is associated with a fundamental change in the elec-
tron density exp. A gradual increase of the average number of the short Mn-O lengths.

Figure 3 shows the real part of the reduced optical conductivity, derived by subtracting the electronic background at different temperatures: Successive curves are offset by 40 Ω⁻¹ cm⁻² for clarity.

display a broad peak at ~5000 cm⁻¹ near $T_C \approx 307$ K) with theoretical calculations of Ref. 9, we obtain a crude estimate of $t \sim E_{JT} \approx 0.3$ eV for La$_{0.67}$Ca$_{0.33}$MnO$_3$ single crystals. In accordance with the theory, the temperature-dependent spectral weight $N_{eff}$ is proportional to the kinetic energy of mobile carriers. In the FM state, the effective hopping amplitude $t^{eff}(m)$ is dependent on the normalized magnetization $m = M/M_s$, and may be approximated by the expression $t^{eff}(m) \approx t(q(m)) \equiv t/(1 + m^2)$. Using a saturated magnetization $M_s \approx 3.9 \mu_B$ for La$_{0.67}$Ca$_{0.33}$MnO$_3$ and the empirical magnetization data $M(T)$ of the sample, the resultant temperature-dependent $m$ and $q(m)$ are illustrated in the inset of Fig. 2, along with $N_{eff}$. This comparison of $N_{eff}$ and $q(m)$ shows that the decrease in $N_{eff}$ with temperature cannot be entirely accounted for by the temperature dependence of $t^{eff}(m)$ alone. We may consider another temperature-dependent factor for $N_{eff}$ due to the JT-induced suppression of the DEX interaction. This factor, estimated by the expression exp$\left(-E_{JT}t^2(h\omega_{ph})^2\right)$ with $\omega_{ph}$ being a characteristic phonon frequency, is independent of the magnetization, unlike $t^{eff}(m)$. Combining the temperature dependence of both $q(m)$ and the exponential suppression factor, we obtain a consistent description for the spectral weight $N_{eff}(T)$ at temperatures below $T_C$, as shown by the dashed line in the inset of Fig. 2, with a reasonable fitting parameter $E_{JT}/(h\omega_{ph})^2 \approx 1/(0.045 \pm 0.005)$ eV. Despite good agreement between our data and the theoretical analysis of Millis et al. at $T < 250$ K, we note that $N_{eff}(T)$ begins to decrease faster with temperature than the theoretical prediction as $T$ becomes closer to $T_C$. A sharp drop of $N_{eff}$ at $T_C$ suggests that the FM metal–PM insulator transition in the CMR man- ganites is associated with a fundamental change in the electronic configuration, which results in a significant shift in the spectral weight, from intraband excitations near the Fermi level in the FM state to effectively interband excitations in the PM state, the latter involving an excitation energy of the order of the Hund’s rule exchange energy.

Figure 3 shows the real part of the reduced optical conductivity at phonon frequencies, derived by subtracting the electronic background at different temperatures. The TO phonon spectra are represented by three sets of splitted bands and fitted by six Lorentzian line shapes (Fig. 4). The magnetic-field effect on the optical conductivity is studied by measuring the far-IR reflectivity spectra under a wide range of magnetic fields (0–16 T). A gradual increase in the reflectivity for the entire far-IR frequency range is observed as the external magnetic field increases from 0 to 16 T and for all temperatures above $T_C$ as shown in Figs. 4(a) and 4(b) for 307 and 330 K. To compare the temperature and magnetic-field effect in detail, we consider representative spectra shown in Figs. 4(c) and 4(d). The reference optical conductivity spectrum in zero field and for a constant temperature is presented by the lower solid curve in each panel. The upper solid curve represents the spectrum taken in the maximum field $H = 16$ T and at a temperature equal to that of the reference spectrum. The dashed curve in each panel corresponds to the optical conductivity spectrum at a temperature lower than that of the reference spectrum, with the same low-frequency limit as the upper solid curve. First, we note that in the vicinity of $T_C$, i.e., at $T = 307$ K, see Fig. 4(c), the effect on enhancing the optical conductivity due to an external magnetic field (16 T) is found to be comparable
to that due to decreasing the temperature (by $\Delta T = 17$ K) in the entire far-IR frequency range. We estimate that the corresponding dimensionless scaling factor $k_B \Delta T / \mu_B H$ gradually changes with increasing temperature from $\approx 1.6$ at $T_C$ to $\approx 2.5$ at $T = 330$ K, as follows from Figs. 4(c) and 4(d). We also note the significant increase of $\sigma(\omega)$, as illustrated in Figs. 4(a)–4(d), with the increasing magnetic field. The magnetoconductivity, as large as about 50% at 5 T in the vicinity of the Curie temperature, is observed and may be referred to as an optical CMR effect.

In summary, we find that the optical conductivity spectra of a La$_{0.67}$Ca$_{0.33}$MnO$_3$ single crystal manifest a crossover from the Drude-like to a hopping conductivity below the FM to PM phase transition. The spectral features are in good qualitative agreement with recent theoretical predictions based on the interplay between the double-exchange mechanism and the Jahn-Teller type electron-phonon coupling. The optical conductivity and the dc magnetization and resistivity data are consistent with a moderate effective electron-phonon coupling. A large optical magnetoconductivity at the phonon frequencies is reported.

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17 The low-frequency optical conductivity may be approximated by the expression $\sigma(\omega \rightarrow 0) = \omega_p^2 / (4 \pi \gamma)$, and $\omega_p^2 \sim 1/m^*$. We attribute the small value of $\sigma(0) \approx 2000$ cm$^{-1}$ to the overdamping in the system, with $\omega_p / \gamma \sim 4.5$, rather than to a large effective mass $m^* \sim 80m_e$ as reported in Ref. 13.