Giant Magneto-Resistance in Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ at Optical Frequencies

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Abstract

The optical properties of Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films have been studied from 5 meV to 25 meV and from 0.25 eV to 3 eV, at temperatures from 15 K to 300 K and magnetic fields up to 8.9 T. A large transfer of spectral weight from high energy to low energy occurs as the temperature is decreased below 180 K, where the dc resistivity peaks, or as the magnetic field is increased. The optical data are found to be consistent with models that include both the double exchange interaction and the dynamic Jahn-Teller effect on the Mn$^{3+}$ $e_g$ levels.

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The recent discovery of colossal magneto-resistance (CMR) in hole-doped ferromagnetic manganite materials of the form \((\text{Ln})_{1-x} (\text{A})_x \text{MnO}_3 - d\), where \(\text{Ln}\) is a lanthanide and \(\text{A}\) is an alkaline-earth element, has revived interest in this complex magnetic system [1]. A decrease in resistance of more than 99% has been observed at temperatures of \(\approx 150\ \text{K}\) and fields of \(\sim 8\ \text{T}\) in thin films of \(\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) [2]. Strong coupling between the electronic and ionic degrees of freedom leads to a static Jahn-Teller (J-T) distortion of \(\text{LaMnO}_3\) and a magnetic-field induced structural phase transition in \(\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3\) [3]. Also, in a recent optical reflectivity study of \(\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3\) [4], a large transfer of spectral weight from high frequencies to low frequencies is observed as the sample is cooled from the paramagnetic state through the Curie temperature, and explained by optical selection rules within a double-exchange picture [5] of the ferromagnetic state. However, a recent theoretical work has pointed out shortcomings of this simple picture and suggested the important role of dynamic J-T distortions [6] in the lattice in order to fully explain the transport properties of CMR manganites.

In this paper we present transmittance and reflectance measurements of \(\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) thin films as a function of both temperature and magnetic field. Our results also show large shifts in spectral weight from above 1 eV to lower energy as the temperature is lowered below 180 K, or as the magnetic field is increased, demonstrating a broadband change in electronic properties at energies several orders of magnitude larger than either \(\mu_BgH \approx 1\ \text{meV}\) or \(k_B T\). In contrast to \(\text{La}_{0.825}\text{Sr}_{0.175}\text{MnO}_3\), the optical properties of \(\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) show evidence for combined double-exchange and dynamic J-T effects.

The samples used in this study were \(\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) thin films grown on \(\text{LaAlO}_3\) and \(\text{Al}_2\text{O}_3\) substrates by pulsed laser deposition in an \(\text{N}_2\text{O}\) atmosphere [4]. The films are epitaxial as revealed by x-ray diffraction, and show 3 MeV \(\text{He}^+\) ion Rutherford backscattering channeling spectra with a minimum yield of 3.8%, indicating a high degree of crystallinity. For the sample discussed below, grown on an \(\text{Al}_2\text{O}_3\) substrate, the room temperature dc resistivity measured with a four-probe method was \(2 \times 10^{-3}\ \Omega\cdot\text{m}\). The maximum resistivity, at 180 K, was \(2.4 \times 10^{-2}\ \Omega\cdot\text{m}\).
Transmittance and reflectance measurements were performed with a combination of Fourier transform spectrometers and grating monochromators to cover the investigated regions of 5 meV to 25 meV and 0.25 eV to 3 eV. High magnetic field transmittance measurements in the Faraday geometry were made with a 9 T superconducting solenoid, using either a lightpipe or optical fiber to gain access to the bore of the magnet. The combined relative uncertainty in the absolute transmittance is ±5% from 5 meV to 25 meV and ±8% from 0.25 eV to 3 eV. (Two standard deviations are used in reporting uncertainties in this paper.) The relative uncertainty in the reflectance spectra is estimated at ±6%.

Transmittance and reflectance spectra at zero magnetic field from 15 K to 300 K for a 140 nm ±10 nm thick Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ film on a 0.5 mm thick Al$_2$O$_3$ substrate are shown in Fig. 1. The inset in Fig. 1(b) shows the low frequency transmittance of this film from 15 K to 240 K, relative to a blank Al$_2$O$_3$ substrate. The free-carrier absorption is very weak in this sample, which is clear from the strong phonon feature that appears at 21 meV. Since the low-frequency transmittance of the film is different from 1 by less than 35%, we can expand the standard sheet conductance formula to linear terms in conductivity, $\sigma$, and find that

$$T_{FS}/T_S \approx 1 - \frac{2Z_0\sigma_1d}{n+1}. \quad (1)$$

Here $T_{FS}$ and $T_S$ are the transmittance of the film/substrate and substrate, respectively, $n = 3.5$ is the index of refraction of the substrate, $d$ is the film thickness, $\sigma_1$ is the real part of the film conductivity, and $Z_0 = 377 \ \Omega$ per square is the impedance of free space. Thus, the low-frequency transmittance values can be used to directly obtain the low-frequency conductivity.

The room temperature conductivity at 5 meV is approximately 10 times larger than the measured dc value of this sample, indicative of the granular nature of the conductance in this type of thin film material. The 5 meV conductivity has a minimum as a function of temperature at 180 K, showing the same trend as the dc conductivity. Similar behavior has been found for the microwave conductivity of these materials [7]. Also, the conductivity
increases as a function of frequency, showing no evidence of a Drude-like roll-off.

The conductivity from 0.25 eV to 3 eV is obtained from the transmittance and reflectance curves shown in Fig. 1 by numerically inverting the exact Fresnel formulas for a thin film on a thick substrate, treating the film coherently and the substrate incoherently \[9\]. The combined uncertainty in the derived conductivity values, which is dominated by the uncertainty in the film thickness, is ±20%.

The real part of the optical conductivity at zero field derived from the data in Fig. 1 is shown in Fig. 2. The symbols near the origin show the conductivity at 5 meV, while the solid and dashed curves show the conductivity derived from the high frequency transmittance and reflectance data. The room temperature curve shows an absorption band centered near 1.2 eV, and the beginning of another band beyond the high energy limit of the data. As the temperature is lowered below 180 K, the conductivity at lower energy increases dramatically, while decreasing somewhat at higher energy. At the same time, the peak in the conductivity shifts to lower energy and broadens.

A comparison of the temperature dependence and the magnetic-field dependence of the transmittance is shown in Fig. 3. Fig. 3(a) shows the ratio of the transmittance at a given temperature to that at 180 K, for temperatures below 180 K, and Fig. 3(b) the ratio of transmittance at 8.9 T to that at 0 T over the same temperature range. A striking similarity can be seen between Fig. 3(a) and Fig. 3(b), indicating that the spectral changes upon decreasing the temperature relative to 180 K, or upon increasing the applied field at a given temperature, are due to the change in spin alignment.

The peak in the magneto-transmittance effect is at 180 K, the same temperature as the peak in the dc and 5 meV resistivities. The magnetic-field effect decreases at both lower and higher temperatures, decreasing to about half the peak value by 240 K, and 20% of the peak value by 15 K. The fact that a significant magnetic field dependence persists in this sample down to the lowest measured temperature is an indication of magnetic disorder in the film (or, possibly, of a canted ferromagnetic ground state) as noted by others \[7,8,9\].

To make a more quantitative comparison between the magnetic-field and temperature
dependence of the optical conductivity, we fit the conductivity at zero field with a sum of a
Drude and Lorentzian terms, and use this fit as a basis for fitting the high-field transmittance.
These results are shown in Fig. 4(a) as the fitted change in $\sigma_1$ at 180 K between 8.9 T and
0 T, compared to the difference between the measured zero-field $\sigma_1$ at 15 K and 180 K,
in Fig. 4(b). The similarity of the two curves reaffirms the conclusion that the changes in
conductivity induced by lowering the temperature or raising the magnetic field are driven
by the spin polarization of the system.

It is interesting to compare our observed optical conductivity versus temperature, shown
in Fig. 2 with other available optical data on rare-earth manganites. At room temperature,
the conductivity in single-crystal $La_{0.825}Sr_{0.175}MnO_3$ has a broad peak at 1 eV and falls off
almost linearly to a small dc value. In the ferromagnetic state, spectral weight is transferred
from high frequency to low frequency leading to a nearly flat conductivity up to 2.5 eV. The
transfer of oscillator strength from high to low energy as the spin polarization is increased
has been interpreted as the suppression of optical charge transfer transitions between the
lower and upper exchange-split $e_g$ bands, accompanied by an increased Drude conductivity
due to an enhanced site-to-site hopping amplitude, within a Hubbard-like representation of
the double-exchange mechanism.

The scale of the high-frequency conductivity in the two materials is similar. However,
in our case, we do not observe a Drude-like frequency dependence in the low-frequency
conductivity at any temperature. Our data is dominated by a peak in the conductivity,
which decreases in spectral weight and shifts to higher energy as the temperature is raised
through the magnetic phase transition. Also, the room temperature conductivity at 5 meV
in our sample is a factor of 5 lower than in the single crystal $La_{0.825}Sr_{0.175}MnO_3$. Lower
values of the dc conductivity in the Nd versus La systems have been noted in dc transport
studies and are believed to indicate an intrinsic difference in the conductivity of the two
alloys.

The qualitative effect of transfer of oscillator strength from high frequency to low fre-
quency as a function of spin polarization appears to be characteristic of CMR manganites;
we have found a magneto-optical response very similar to that shown in Fig. 3(b) in a La$_{0.7}$Ba$_{0.3}$MnO$_3$ film at 240 K. This sample has a measured dc resistivity about 2 orders of magnitude smaller than the Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ film, and shows almost no magneto-optic response at low temperature, consistent with a nearly saturated ferromagnet.

In the inset to Fig. 2 we show the temperature dependence of the oscillator strength expressed in terms of the effective electron density

$$N_{eff}(\omega) = \frac{2V_{cell}m}{\pi e^2} \int_0^\omega \sigma_1(\omega')d\omega'$$

(2)

integrated to 1.5 eV (where $\Delta \sigma = 0$). $V_{cell}$ is the unit cell volume. It is apparent from both Fig. 2 and Fig. 4 that the oscillator strength sum rule is not satisfied over the range of photon energies that we have investigated. As the temperature is lowered, the oscillator strength above 1.5 eV decreases, but more slowly than the growth at lower frequency (and more slowly than is found in La$_{0.825}$Sr$_{0.175}$MnO$_3$). Thus, the magnetic field and temperature dependence must extend to higher energies.

The increase of the spectral weight of the peak near 1 eV as the temperature is lowered below $T_c$ shows that this feature cannot be due simply to d-d transitions between spin-split Mn $e_g$ levels. On the other hand, its strong temperature and magnetic-field dependence implies that it must involve the $e_g$ states in an important way. Indeed, both the initial and final states must have a large $e_g$ component. If, for example, the absorption peak was due to transitions from the O(2p) states to the $e_g$ states, then both O(2p) spins would participate, and the transition would not depend on the orientation of the Mn core spins. Moreover, the magnetic field dependence means that the transition is sensitive to the relative alignment of two adjacent core spins. Thus, we conclude that the main component of the conductivity peak is a charge transfer transition between the $e_g$ levels of two adjacent sites. For the case where the final state is on an already occupied site (as in LaMnO$_3$), the transition energy would be shifted to well above the investigated region by the on-site Coulomb energy $U \approx 4$ eV. Therefore, we conclude that it must be due to the charge transfer transition from a Mn$^{3+} e_g$ level to the unoccupied Mn$^{4+} e_g$ levels on an adjacent site.
Millis, Mueller, and Shraiman [11] suggest that this conductivity peak is to be interpreted as the transition from a lower dynamic Jahn-Teller split Mn\(^{3+}\) e\(_g\) level to the unsplit Mn\(^{4+}\) e\(_g\) levels of a neighboring site. In their model, which includes both double-exchange and J-T polaron effects, the splitting depends on the ratio of the Jahn-Teller self-trapping energy to the e\(_g\) bandwidth [6,11]. As the spins align, the double-exchange-driven hopping probability increases, leading to an increased e\(_g\) bandwidth and thus a decrease of the J-T splitting. The transition energy is expected to be larger than half of the J-T splitting because of the difference between the centers of gravity of the e\(_g\) levels on the Mn\(^{4+}\) and Mn\(^{3+}\) ions. Optical conductivity curves calculated within this model show shifts in oscillator strength, linewidth, and peak position versus temperature which are similar to the data in Fig. 2 [11].

Optical transitions involving O(2p) orbitals are also expected in the spectral range from 0.25 eV to 3 eV, as suggested by others [4,9]. Therefore, the 1.2 eV peak in Fig. 2 could contain contributions from several optical transitions. However, as argued above, these transitions would not have the observed temperature and magnetic field dependence. Appropriate measurements and systematic doping studies will be required to properly differentiate the various contributions to the optical conductivity.

It is interesting to reconsider the differences between Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) and La\(_{0.825}\)Sr\(_{0.175}\)MnO\(_3\) within the double-exchange/J-T polaron model. The smaller ion size for Nd (compared with La) leads to greater Mn-O-Mn bond angle distortions, so that a stronger J-T coupling is expected for Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) [12]. This is expected to lead to a larger J-T gap. Therefore, it appears that the difference in the low-temperature behavior of the transport and optical properties of the two materials can be understood in terms of a finite J-T gap in Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) and a near zero gap in La\(_{0.825}\)Sr\(_{0.175}\)MnO\(_3\). The larger J-T gap may also be responsible for the differing behaviors above 1.5 eV, where the conductivity in Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) has much less temperature dependence. This indicates that satisfying the optical oscillator strength sum rule in the Nd alloy may require a wider frequency range than in the La alloy.

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FIGURES

FIG. 1. Reflectance (a) and transmittance (b) of a 140 nm thick Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ film on Al$_2$O$_3$ at zero magnetic field for various temperatures. The inset in (b) shows the FIR transmittance; in this case the solid line is the transmittance at 240 K rather than 300 K.

FIG. 2. Real part of the optical conductivity, $\sigma_1$, versus photon energy derived from the data in Fig. 1. A large transfer of spectral weight from high to low energy is apparent, along with a shift in the peak to lower energy as the temperature is decreased. Inset: $N_{eff}$ integrated up to 1.5 eV versus temperature.

FIG. 3. Transmittance ratios for temperature (a) and magnetic field (b) for the 140 nm Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ sample. Frame (a) shows the ratio of the transmittance at several temperatures to that at 180 K at zero field, while (b) shows the ratio for $H = 8.9$ T to 0 T at 180 K and below. In frame (b), the solid circle shows the FIR transmittance ratio at 15 K, and the diamond the ratio at 150 K.

FIG. 4. Comparison of (a) the fitted difference $\Delta \sigma_1 = \sigma_1(180K,8.9T) - \sigma_1(180K,0T)$ with (b) the measured difference $\Delta \sigma_1 = \sigma_1(15K,0T) - \sigma_1(180K,0T)$. The change in spectral weight has a similar shape in both cases, with the large increase at low energy implying that the decrease above 1.2 eV must extend to higher energy.
Photon Energy (eV)

Magnetic Field

Temperature

\( \Delta \sigma_1 \left( 10^4 \, \Omega^{-1} \cdot m^{-1} \right) \)

(a)

(b)