Magnetic and optical properties of multiferroic GdMnO$_3$ film

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Abstract

We report on magneto-optical studies of an epitaxial thin film of GdMnO$_3$ grown on SrTiO$_3$. Significant differences were found between the magneto-optical and absorption spectra, which highlight the importance of magneto-optics in determining the magnetic character of the optical transitions. Two main features were identified in the magnetic circular dichroism (MCD) spectra: the charge transfer transition between Mn $d$ states at ~2eV and the band edge transition from the oxygen $p$ band to the $d$ states at ~3eV. The strength of the MCD at ~2eV correlates well with the Mn spin ordering, indicating the applicability of magneto-optics for understanding the magnetic properties.

1. Introduction

In recent years there has been great interest in the physics of “multiferroics”. Discovered in the 1970s, these unusual materials exhibit ferroelectric and magnetic ordering simultaneously. These two order parameters have strong magnetoelectric coupling, allowing the reversal of the ferroelectric polarization by the application of a magnetic field or the control of the magnetic order parameter by an electric field. Together with recent unprecedented progress in epitaxial thin film growth, this unique property makes these “old” materials very good candidates with which to construct multifunctional spintronic devices [1, 2].

In this paper we report magneto-optical measurements on the orthorhombic multiferroic manganite GdMnO$_3$. This material exhibits several magnetic phase transitions as the temperature is lowered. First, magnetic frustration due to competing exchange integrals between successive neighbours stabilizes a spiral magnetic phase below the Néel temperature $T_N$ =47K [3-5]. Next there is a lock-in transition to a canted A-type antiferromagnetic phase at 19K for GdMnO$_3$. At even lower temperatures, the Gd moments order and the oxygen atoms are pushed off the Mn-Mn bond, driving an electric polarization. It is thus clear that the charge, spin, orbital, and lattice subsystems are linked very tightly in this material, making their investigation by magneto-optical techniques particularly interesting.

We focus particularly on a spectral feature at ~2 eV. In LaMnO$_3$ this peak is observed clearly in the absorption spectrum and is attributed to a charge transfer excitation between neighbouring Mn ions. However, the peak is suppressed in absorption for heavier rare earth manganites including GdMnO$_3$ [6-9]. This reduction in intensity has been related to the different canting of the Mn $d$-orbitals and also to the directions of Mn spins. In our work we find that the charge transfer peak appears very prominently in the magnetic circular dichroism (MCD) spectra, which allows us to correlate the magneto-optical properties with the magnetization as the temperature is lowered through the magnetic transitions. We find that the strength of the peak correlates with the Mn spin ordering, thus confirming the strong magnetoelectric coupling of GdMnO$_3$.

2. Sample preparation and magnetic characterisation

Epitaxial thin film samples of GdMnO$_3$ were deposited on a [110] SrTiO$_3$ substrate using RF magnetron sputtering. SrTiO$_3$ was chosen as the substrate because it facilitated high quality epitaxial thin film growth. However it did have some disadvantages for the optical studies reported here. The
band gap energy at 3.2 eV reduced the useful energy range over which absorption measurements could be made, and the structural transition at ~100K gave rise to birefringence, making magneto-optical measurements more difficult [10].

The targets of GdMnO$_3$ were prepared from stoichiometric mixtures of Gd$_2$O$_3$ and MnO$_2$. GdMnO$_3$ films of thickness of 100-200 nm were sputtered onto single crystal SrTiO$_3$ [110] substrates in an atmosphere of Ar and O$_2$ at a pressure of 1–2 mTorr. The substrate temperature was 650°C. This produced an epitaxial GdMnO$_3$ film with the [110]-direction parallel to the plane of the substrate. X-ray data taken at room temperature are shown in Fig. 1(a), confirming the high crystalline quality.

![Figure 1](image.png)

**Figure 1.** (a) X-ray data showing epitaxial growth, (b) Field cooled (red) and zero field cooled (black) magnetisation data of the film (contribution from STO was subtracted) (c) Magnetic hysteresis loops of the film at 5K and 10K (linear background subtracted.)

The magnetic properties of the films were investigated by SQUID magnetometry with the magnetic field perpendicular to the samples. This geometry was chosen to coincide with the Faraday geometry used for the magneto-optical studies. Field cooled and zero field cooled magnetisation plots are shown in Fig. 1(b). The data were taken in a field of 100 Oe and the contribution from the diamagnetic substrate has been subtracted. We note there is a positive, temperature-independent susceptibility above ~100 K.

Magnetic hysteresis loops were only observed for temperatures below the transition to the canted phase at 19 K. Typical hysteresis loops at 5 K and 10 K are shown in Fig. 1(c), and coercive fields are 250 Oe and 140 Oe at temperatures 5 K and 10 K are deduced. These hysteresis loops were obtained by subtracting off the diamagnetic signal from the substrate and the paramagnetic signal from the film, both of which are linear in the field. As shown in Fig. 1(b), this paramagnetic signal was large at low temperatures, but could be clearly identified from the linear variation of the magnetization for fields in the range 7–10 kOe.

### 3. Optical Measurements

The absorption spectrum of the film was measured at room temperature and is shown in Fig. 2(a). Previous work has identified a strong, electric-dipole-allowed optical transition at the band edge around ~3 eV between the oxygen $p$ states and unoccupied Mn $d$ states. This absorption band is observed in our samples, although it was not possible to make measurements above 3.2 eV due to the absorption of SrTiO$_3$ substrate [11]. (See inset to Fig. 2(a).) Weak absorption at the charge-transfer transition around 2 eV was also observed in the absorption, but without any structure.

Magnetic circular dichroism (MCD) measurements were made using the apparatus described in [12]. The MCD spectrum measures the difference in absorption between left and right circularly polarised light, and thus reflects the magnetic character of the electronic states involved in the optical transition [13]. In our experiments we had to be careful to orient our samples so that the $E$ vector of...
the light was along the optic axis of the substrate, in order to avoid complications due to the birefringence of SrTiO$_3$ below 100 K.

We present two sets of data. In the first, we measured the MCD spectrum in zero magnetic field after having reduced the field to zero from values of ±5 kOe. This gives the spectrum at remanence. In the second, the data were obtained from the difference in the induced ellipticity taken in fields ±$H$ where $H$=5 kOe. This is the standard MCD spectrum and corresponds to the MCD at saturation. In the second type of measurements it was necessary to subtract the contribution from the substrate. This was done by measuring the temperature dependence of the MCD from a blank substrate and subtracting it from the spectra of the GdMnO$_3$/SiTiO$_3$ sample. The SrTiO$_3$ substrate was found to have a large and strongly temperature-dependent circular dichroism just below its band gap, making saturation MCD measurements on the GdMnO$_3$ film difficult in this spectra region. Since the substrate dichroism varied linearly with the magnetic field it did not contribute to the remanent spectrum.

The MCD spectra of the GdMnO$_3$ film at remanence and saturation are compared in Figs 2(b) and 3(a). The remanent spectrum should have the same shape as that taken in field but be scaled by the ratio $M_r/M_{sat}$, where $M_r$ and $M_{sat}$ are the magnetizations measured at remanence and saturation, respectively. This was observed for the signal at ~2 eV at 10 K, but not for the signal near the band edge, where the large paramagnetic signal from the substrate leads to the possibility of errors. The saturation data shown in Fig. 3(a) are therefore only presented for the energy region below 2.3eV where we were confident that there was no contamination from the substrate.

The remanent spectrum at 10 K shown in Fig. 2(a) appears to shows the three spectral components at 1.9, 2.3 and 2.6 eV that were observed in LaMnO$_3$ but only at high temperature [8]. The remanent signal is strong near 2eV and weakens where the interband transition starts at ~3eV. We attribute this to the fact that the transitions near 2 eV correspond to transitions between two magnetic ions, and consequently have much stronger magneto-optic effects than the transitions from the oxygen states to an unoccupied Mn level which only involve one magnetic ion.

![Figure 2](image2.png)

**Figure 2.** (a) The absorption of the film on the substrate, the absorption of a bare substrate is shown in the inset; (b) the MCD signal taken at remanence between 10K and 60K.

The MCD signal is sensitive to magnetic order, making it interesting to study its temperature dependence. Figure 3(b) shows the MCD signal at 2 eV in field over the temperature range 5–300 K. The signal drops off sharply with temperature up to 50 K, and then more slowly to 100 K, following the behaviour of the magnetisation shown in Fig. 1(b). The close correspondence between the MCD at 2 eV and the magnetization gives a clear indication of the magnetic character of the charge transfer transitions between neighbouring Mn ions.
4. Conclusions

We have demonstrated the importance of making MCD measurements at remanence for the understanding of the ordering of the Mn spins in GdMnO$_3$. We find that the charge transfer transition at ~2 eV in GdMnO$_3$ gives a strong signal in the MCD spectrum at remanence, even though it was not visible as a distinct peak in the absorption. The temperature dependence of the charge-transfer MCD signal was found to follow the magnetization. These results clarify the importance of magnetoelectric coupling in determining the magneto-optical properties of multiferroic materials such as GdMnO$_3$.

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