Jahn-Teller contribution to the magneto-optical effect in thin-film ferromagnetic manganites

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We have investigated the magneto-optical response in the visible spectrum of thin-film ferromagnetic manganites. We observe a huge enhancement of the magnetorefractive effect (MRE) around the Curie temperature, which is linked to the colossal magnetoresistance. It is found that the unusually large MRE at visible frequencies is accompanied by an *increase* in the magnetic field of the optical conductivity. We argue that these remarkable phenomena are related to the field-induced suppression of Jahn-Teller dynamical charge localization.

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It is well established that the optical response of metals in the midinfrared (mid-IR) spectrum and below is dominated by intraband electronic excitations of delocalized electrons, giving way to the Drude contribution of the spectral optical response. When magnetic fields are applied, the optical conductivity and refractive index are changed and therefore also the reflectance, giving way to a magnetorefractive effect (MRE).[1] Thus field-induced changes in the reflectance have been used during last years as a means to characterize optically the spin-dependent transport in giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) devices.[2–5] However, in common metals the MRE is vanishingly small for light of frequency above IR, i.e., near the plasma frequency of most metals, where the Drude contribution also vanishes. Nevertheless, at these high frequencies, other sources of MRE, different than the optical response of free electrons, can exist, especially in strongly correlated systems. Indeed, above near-IR, the optical response is usually quite complex in these systems because of the existence of bound-electron resonances which can only be excited with high enough photon energies. Thus MRE at visible and ultraviolet frequencies might be dominated by interband transitions instead of intraband transitions as occurs at IR frequencies.

One particularly interesting case of complex spectral optical response is that of manganites.[6,7] The reason is that within a narrow window of temperatures around the ferromagnetic transition, manganites exhibit dynamic Jahn-Teller (JT) distortions that are at the origin of the colossal magnetoresistance (CMR) phenomenon.[8] Photons with appropriate energies will promote electronic transitions among JT split levels, will be strongly absorbed, and, as a result, will contribute to the optical conductivity. Indeed, the spectral optical response of manganites and its dependence on magnetic field have attracted the attention of many researchers.[6,7,9–12] In particular, since JT distortions are strongly affected by magnetic fields, it is expected that the optical conductivity, and therefore also the dielectric constant and refractive index, may depend significantly with field, giving way to a sizable MRE. As JT resonances are located around 1.5 eV,[9,10] the effect of applied magnetic fields on the electronic structure of manganites can be suitably analyzed by exploring the optical magnetoresponse at energies in the visible spectrum. Thus, exploring MRE response at those wavelengths provides a unique tool to probe electronic correlations in such complex systems.

Here we report on the characterization of the optical magnetoresponse in the visible spectrum of some manganites. From these experiments we inferred directly that the ac conductivity at visible wavelengths *decreases* with field and, therefore, the optical (visible) magnetoresistance is *positive*, in contrast to the negative CMR observed in the dc limit. We discuss this remarkable result in terms of a spectral weight transfer from the JT bound resonance peak toward the Drude peak as we apply a magnetic field. We suggest that this type of experiments might be extended to look into the electronic states of other complex systems and the effect on them of external stimuli other than magnetic fields.

We have investigated the magneto-optical properties of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) thin films grown by radio-frequency sputtering on (110)-oriented $SrTiO_3$ (STO) substrates and also of $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) and $SrRuO_3$ (SRO) films grown by pulsed laser deposition on (001) STO substrates. These films, extensively characterized by x-ray diffraction, were found to be epitaxial with high crystalline quality (see Refs. 13–15 for growth conditions and reports on the structural characterization). The temperature-dependent optical magnetoresponse was characterized by using a laser diode having a wavelength $\lambda = 650$ nm. We discuss here magneto-optical experiments performed in transverse configuration [Fig. 1(a)]. In contrast to longitudinal and polar geometries, in which the rotation of the polarization plane and ellipticity are measured, in transverse geometry we measure the changes in field of the intensity of the reflected light; thus we had access not only to Kerr effects but also to MRE. We have followed the null-

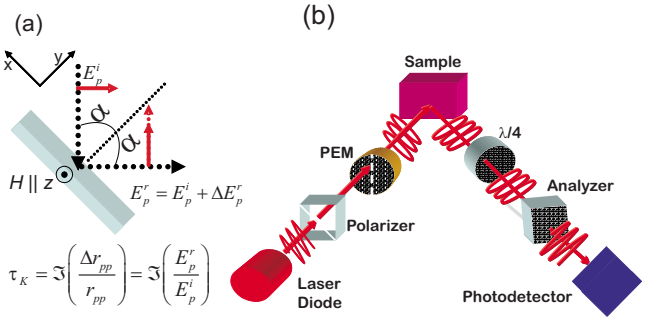

FIG. 1. (Color online) (a) Geometry of the transverse Kerr measurements. (b) Sketch of the magneto-optical setup.

ellipsometry method proposed by Postava *et al.*[16] to determine the reflection coefficients. Figure 1(b) shows schematically the basic components of this setup. The light from the laser source goes through a polarizer, which is rotated 45° with respect to the modulator axis of a photoelastic modulator (PEM). The retardation angle of the PEM is an oscillatory function of time $\varphi=\varphi_0+\varphi_A \sin[\Omega t]$, where Ω is the angular frequency of the PEM phase oscillation, φ_A denotes the modulation amplitude, and φ_0 corresponds to the residual birefringence due to PEM internal stress. After reflection on the sample surface, the light goes, through a quarter-wave compensator (set at an azimuth of +45°), toward an analyzer (its azimuth was adjusted at $\Delta+\pi/4$ to have the initial null condition for I_Ω—see below—at zero magnetic field[16]). The intensity signal finally collected at the detector is given by[16]

$$I=\left[I_0+J_0(\varphi_A)\frac{I_{2\Omega}}{2J_2(\varphi_A)}\right]+I_\Omega \sin[\Omega t]+I_{2\Omega}\cos[\Omega t]. \tag{1}$$

The first addend corresponds to the nonmodulated part, where I_0 is the background intensity (measured with a dc multimeter) and $J_0(\varphi_A)$ and $J_2(\varphi_A)$ are the Bessel functions of the first kind. We set the PEM modulation amplitude to $\varphi_A=137.79°$, for which $J_0(\varphi_A)=0$, so that the first term of Eq. (1) was reduced to I_0. The second and third terms of Eq. (1) are proportional, respectively, to the first (I_Ω) and second ($I_{2\Omega}$) harmonics of the intensity recorded at the detector, which are easily extracted by synchronizing a lock in to the frequency of the PEM (Ω). We report here on measurements of the imaginary part of the transverse Kerr ($\tau_K=\mathrm{Im}[\frac{\Delta r_{pp}}{r_{pp}}]$). Note that τ_K is essentially related to the change in magnetic field of the reflectance and is obtained from[17]

$$\tau_K \approx \frac{I_\Omega}{2J_1(\varphi_A)I_0 \sin 2\Psi}, \tag{2}$$

where $J_2(\varphi_A)$ is the Bessel function and Ψ (and Δ) are the ellipsometric angles obtained experimentally from the amplitude reflection coefficients of *s*- and *p*-polarized lights through the expression $\frac{r_{pp}}{r_{ss}}=\tan\Psi e^{i\Delta}$.[18]

Using this approach the τ_K signal of the LCMO film has been measured as a function of temperature (10–300 K) and magnetic field for light at an incidence angle $\alpha=45°$ [see Fig. 1(a)]. Some illustrative results are collected in Fig. 2. In these figures we plot the hysteretic loops of τ_K measured at different temperatures: $T=160$ K [Fig. 2(a)], $T=245$ K [Fig. 2(c)], and $T=255$ K [Fig. 2(e)]. We see that at $T=160$ K, well below the Curie temperature $T_C\approx260$ K, τ_K is almost an odd function of the magnetization and it saturates at high enough fields [Fig. 2(a)]. We stress here that this is just what is expected from Kerr effects, which are proportional to the magnetization. However, as we approach the transition temperature the transverse Kerr signal τ_K clearly shows that, superimposed to the usual odd-in-magnetization contribution, there is an additional even-in-magnetization magneto-optical contribution [Figs. 2(c) and 2(e)]. To separate both contributions, we have decomposed the τ_K signal into even and odd components by using $\tau_K^{\mathrm{odd}}=1/2[\tau_K(H)-\tau_K(-H)]$ and $\tau_K^{\mathrm{even}}=1/2[\tau_K(H)+\tau_K(-H)]$. In Figs. 2(b), 2(d), and 2(f) we collect the results corresponding to data of panels 2a, 2c, and 2e, respectively. To make the τ_K^{odd} and τ_K^{even} data clearer, we have only considered in Figs. 2(b), 2(d), and 2(f) the ascending branch of the $\tau_K(H)$ loop and, thus, hysteresis is no longer visible in these plots. As expected, the odd component τ_K^{odd} shows the typical shape of a magnetization loop, with maximum (saturation) amplitude which is the largest at low temperatures [Fig. 2(b)] and decreases gradually when approaching T_C [Figs. 2(d) and 2(f)]. In contrast, we observe that τ_K^{even} is very small at low temperatures [Fig. 2(b)], whereas close to T_C τ_K^{even} is larger than the odd counterpart by more than an order of magnitude [Fig. 2(f)].

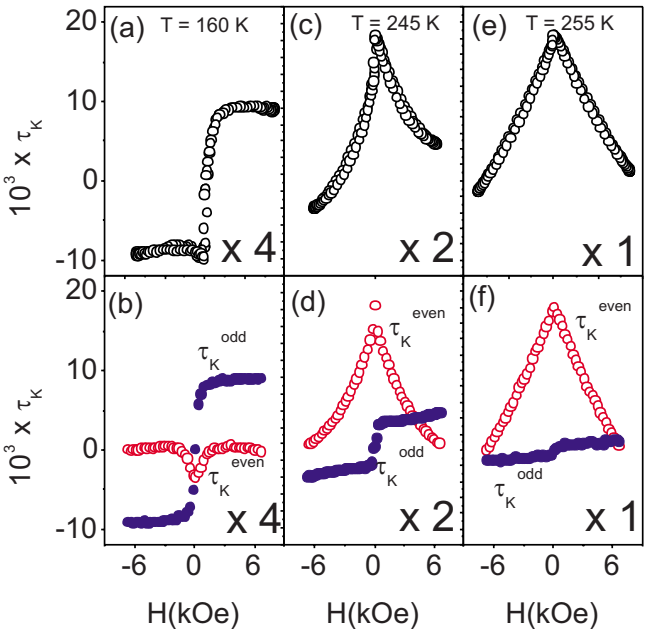

FIG. 2. (Color online) The imaginary transverse Kerr signal τ_K of the LCMO film (at incidence angle $\alpha=45°$) is plotted vs the magnetic field at temperatures (a) $T=160$ K, (c) $T=245$ K, and (e) $T=255$ K. The corresponding odd (τ_K^{odd}) and even (τ_K^{even}) components are plotted in (b), (d), and (f). Data have been magnified by a factor 4 in (a) and (b) and by a factor 2 in (c) and (d).

Close inspection of Figs. 2(b), 2(d), and 2(f) reveals more details about the even response. We see in Fig. 2(b) that at low temperature ($T=160$ K) τ_K^{even} is negative and saturates at the same value at which the magnetic loop saturates. This means that the field dependence of τ_K^{even} at low enough temperature is closely correlated with the magnetization. The most probable source of τ_K^{even} at these temperatures is the second-order Kerr effect, which depends on quadratic components of the magnetization.[19] However, the situation is radically different as the Curie temperature is approached ($T=245$ and 255 K). Now we see that τ_K^{even} is much larger and positive and, more important, it does not saturate [Figs. 2(d) and 2(f)]. Therefore, close to T_C, the behavior of τ_K^{even} is not correlated with the magnetization loop, indicating that contributions other than the Kerr effects are at its origin. This conclusion is reinforced by the results of the experiments that will be described below.

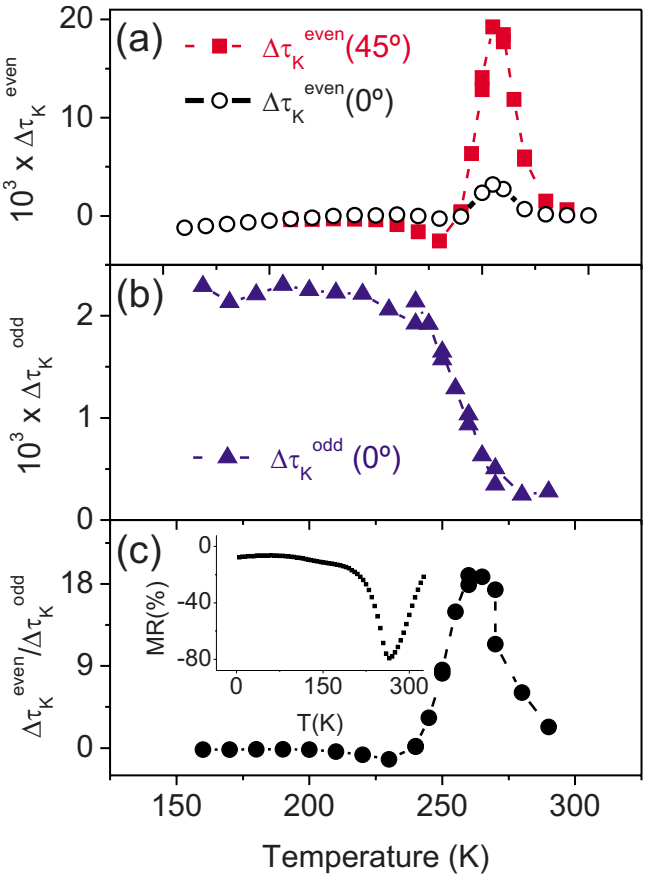

FIG. 3. (Color online) Temperature dependence of (a) $\Delta\tau_K^{even}$, (b) $\Delta\tau_K^{odd}$, and (c) $\Delta\tau_K^{even}/\Delta\tau_K^{odd}$, all measured at an incidence angle $\alpha=45°$. The even and/or odd components of the transverse Kerr are defined as $\Delta\tau_K^{odd,even}=\tau_K^{odd,even}(H_{max}=0\ \text{kOe})-\tau_K^{odd,even}(H_{max}=7\ \text{kOe})$. Panel (a) also includes $\Delta\tau_K^{even}$ measured at normal incidence $\alpha=0°$. The inset of panel (c) shows the temperature dependence of the magnetoresistance MR defined as $MR=[R(H=80\ \text{kOe})-R(H=0)]/R(H=0)$.

We have quantified the odd and even contributions by evaluating $\Delta\tau_K^{odd,even}=\tau_K^{odd,even}(H_{max}=0\ \text{kOe})-\tau_K^{odd,even}(H=7\ \text{kOe})$, where $H_{max}=7$ kOe is the maximum magnetic field applied in the experiment. The overall temperature dependences of $\Delta\tau_K^{odd}$ and $\Delta\tau_K^{even}$ are depicted in Fig. 3. From these measurements we see that the temperature dependence of $\Delta\tau_K^{odd}$ [Fig. 3(b)] follows that of the magnetization, whereas $\Delta\tau_K^{even}$ [Fig. 3(a)] has a strikingly similar temperature dependence as the CMR [see the inset of Fig. 3(c)]. We strengthen that, as illustrated by data in Fig. 3(c), the MRE response ($\Delta\tau_K^{even}$) of the LCMO films is about a factor ≈ 20 larger than the corresponding Kerr signal ($\Delta\tau_K^{odd}$) at temperatures close to T_C.

That the huge enhancement of the magneto-optical response near T_C is uncorrelated with Kerr effects is further confirmed by measurements in the transverse geometry with p-polarized light at normal incidence, i.e., with $\alpha=0°$ instead of $\alpha=45°$. For symmetry reasons, the transverse Kerr response is forbidden in this configuration. As shown in Fig. 3(a), still an enhancement of τ_K^{even} at $\alpha=0°$, albeit lower than that measured at $\alpha=45°$ is clearly visible close to T_C [the reduction is related to the change in reflectance with α (Ref. 20)]. We have also checked that the slope $\delta\tau_K^{even}/\delta M$ and the magnitude of the effect are not modified when the in-plane field orientation is changed (not shown).

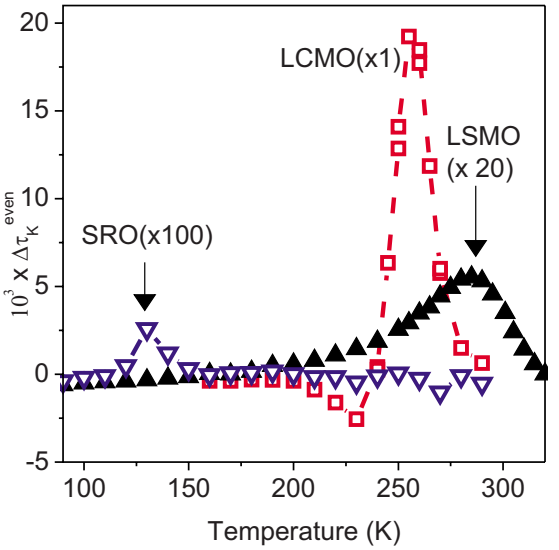

FIG. 4. (Color online) Temperature dependence of the even component of the transverse Kerr $\Delta\tau_K^{even}=\tau_K^{even}(H_{max}=0\ \text{kOe})-\tau_K^{even}(H=7\ \text{kOe})$ for films of LCMO, LSMO (magnified by a factor 20), and SRO (magnified by a factor 100).

We have investigated the link between the MRE enhancement and the CMR physics by measuring τ_K of other ferromagnetic oxides. One of them (LSMO) is a CMR system with weaker electron-phonon and JT coupling and $T_C \approx 350$ K, whereas in the other (SRO, $T_C \approx 140$ K) Ru^{4+} is not a JT ion and thus SRO does not exhibit JT instabilities. In Fig. 4 we show the temperature dependence of $\Delta\tau_K^{even}$ for all three samples (LCMO, LSMO, and SRO): we see that it is virtually zero everywhere except a narrow window around T_C for all films. However the amplitude of the signal varies largely: it is the highest for the LCMO film, whereas for SRO the signal is almost 3 orders of magnitude lower than that of LCMO, as it might be expected from the significantly smaller MR of SRO (Ref. 21) with respect to manganites.[8] Finally, the LSMO film shows an enhancement of τ_K^{even} but it is much smaller than that observed in LCMO. These experiments indicate that the CMR physics and JT coupling are basic ingredients for the enhancement of the MRE reported here.

We note that the data of Figs. 2(c) and 2(e) indicate that the even component τ_K^{even} (and therefore the reflectance) decrease with field, i.e., $\tau_K^{even}(H)<\tau_K^{even}(0)$. Therefore, this signals a reduction in the conductivity with the field at visible frequencies. Indeed, we have verified that the background intensity I_0 [Eq. (1)] measured in zero field, which is also a measure of the reflectance, has a maximum near the Curie temperature (not shown), i.e., the reflectance is the *highest* at the temperature at which the dc conductivity is the *lowest* (see also Figs. 3 and 4). This is a rather counterintuitive result if we recall that the dc magnetoresistance is largely negative [inset of Fig. 3(c)] and we would expect an increase in reflectance with field. Our observation is in agreement

with optical spectra of other manganites measured above IR frequencies.[6,9] We attribute this phenomenon to a spectral weight transfer from high to low frequencies, as discussed by Jung *et al.*[9,10] The physics behind this phenomenon is linked to the high sensitivity of JT resonant transitions to applied external magnetic fields. For temperatures approaching the magnetic transition, the incoming visible light interacts strongly with the JT resonance and gives way to a peak contribution to the optical conductivity. When a magnetic field is applied, JT distortions are strongly suppressed and a substantial spectral weight is transferred to low frequency.

Bound-electron resonances associated to the electron-phonon coupling are a quite general phenomenon in oxides. The relevant energy scales are typically of the order of the eV and, thus, within the range of near-IR, visible and ultraviolet frequencies. As a result, we emphasize that the methodology described in this work may prove very useful to give an additional insight into the nature of some structural and electronic transitions driven by magnetic/electric fields or by temperature. Particular examples are charge order/disorder transitions in manganites[8] or magnetic transitions in titanates.[22] In these materials the roles of the orbital order/disorder and consequently of the electron-phonon coupling might be clarified by inspection of the spectral optical response upon application of magnetic/electric fields or analyzing spectra as a function of the temperature.

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