Chapter 5

Dielectric properties of the TbMnO$_3$ films

5.1 Abstract

In an effort to confirm or exclude the presence of ferroelectricity in the films and to characterize the magnetoelectric behaviour of the films, measurements of the dielectric constant and magnetocapacitance were performed. We show that the dielectric anomaly that indicates the paraelectric-ferroelectric phase transition is absent for films having a thickness below 70nm and is recovered for thicker films with a bulk-like relaxed part. A relaxation mechanism, involving polaron hopping, could be observed at around and below 1kHz. A second relaxation mechanism occurs at higher frequencies in the 40nm film and is attributed to the relaxation of domain walls. The data of the partially relaxed 90nm film suggests that the relaxation of domain walls is shifted to higher frequencies, pointing to a clamping effect of domain walls for the thinner films. Moreover, at high frequencies, the 90nm film shows a small magnetocapacitance effect of around 1%, whereas a magnetoresistance effect as high as $\approx 150\%$ could be measured under an applied in-plane field of 60 kOe, at 15K. These results indicate an interface-dominated positive magnetoresistance, possibly associated with the domain walls or grain boundaries. At lower frequencies, a core-dominated positive magnetoresistance is observed. We show here the crucial role of domain walls and grain boundaries on the dielectric properties of the films.
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5.2 Introduction

The structure and magnetic properties of TbMnO$_3$ thin films on SrTiO$_3$ have been studied in the previous chapters and have shown that the films have a tetragonal structure for very low thicknesses ($\approx$2nm) and, for increasing thickness, they gradually change into an orthorhombic structure, less distorted than the bulk one, by modifying the in-plane lattice parameters, $a_0$ and $b_0$. However, with increasing the thickness of the films, the out-of-plane lattice parameter remains constant, indicating that the strain is maintained for thicknesses up to about 70nm (for films grown under 0.9mbar of oxygen). For thicker films, a coexistence of a strained and a relaxed part (with bulk-like lattice parameters) is found. Varying the oxygen pressure during growth (from 0.9mbar to 0.25mbar) did not seem to affect the magnetic properties of the films: dominant antiferromagnetic response with the signature of ferromagnetic interactions and an increase of the field-cooled induced magnetic moment with decreasing thickness. In addition, no anomaly could be detected in the magnetization curve corresponding to the transition to the spin cycloidal state (which induces the ferroelectric phase), as in bulk. Considering that the overall strain state is constant and looking at the TEM images shown in Chapter 3, which show a linear increase in the domain wall density with decreasing thickness, we have proposed that the ferromagnetic interactions originate at the domain walls.

In the past few years, many new multiferroics and magnetoelectric materials have been discovered and intensively studied. However, unreasonable dielectric and ferroelectric properties have been often reported due to a lack of knowledge of both the material investigated and the measurement technique. It has been shown that extrinsic contributions can give rise to a false large and frequency-dependent dielectric constant and can even give rise to magnetocapacitance effects. Moreover, leaky samples can display hysteresis effects in polarization measurements that can be mistaken for intrinsic ferroelectric properties of the material under study [142–144].

In the following experiments we investigate the dielectric properties of the TbMnO$_3$
films to confirm or exclude the presence of a ferroelectric transition. Indeed, a dielectric anomaly is found in the bulk material at the lock-in/ferroelectric ordering temperature ($T_f \approx 27K$). To find out if the ferroelectric ordering is suppressed by the strain, a film showing only a strained part (40nm) and a film showing strained and relaxed parts (90nm) were chosen. Moreover, performing an impedance spectroscopy study of the thin films, we can correlate the measurement of the capacitance and the dielectric loss with relaxation processes occurring in the films and separate the intrinsic and extrinsic effects. Dielectric measurements under magnetic field will give insight into the magnetoelectric behaviour of the films.

5.3 Experimental

TbMnO$_3$ thin films were deposited on conductive Nb-SrTiO$_3$ (001) (1% doped) using RHEED-assisted Pulsed Laser Deposition (PLD). Nb-SrTiO$_3$ was used as a bottom electrode because the films grown on SrRuO$_3$//SrTiO$_3$ were (110)-oriented, different from those grown on bare SrTiO$_3$ (which show a (001) orientation) discussed earlier. This can be seen in figure 5.1, where an AFM image (a) and a x-ray 2θ-ω scan (b) around the (001) reflection of the SrTiO$_3$ substrate are shown. Although the topography of the surface is comparable to that of the films grown on a bare substrate, the x-ray diffraction data show a different diffractogram. Indeed, the peak corresponding to the film is seen on the left-hand side of the substrate peak, whereas films on a bare substrate had a peak on the right-hand side of the substrate. The evaluation of the out-of-plane lattice parameter for the TbMnO$_3$ layer reveals that the film is (110)-oriented.

A 40nm and a 90nm film were grown on Nb-SrTiO$_3$ under the same optimized conditions as those used for the growth on undoped SrTiO$_3$. The morphology of the films was studied using Atomic Force Microscopy (AFM), whereas the structure of the films was studied using x-ray diffraction. After structural characterization, SrRuO$_3$ top electrodes were deposited ($600^\circ$C, $8.10^{-3}$mbar, 2Hz) by using PLD and a mask. The elec-
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Figure 5.1: (a) AFM picture for a 40nm TbMnO$_3$ film on a 10nm SrRuO$_3$ bottom electrode on (001)SrTiO$_3$ substrate. (b) 2θ-ω diffractogram of the corresponding film. The experimental data are shown as black line whereas the fit to the data is shown as a grey line.

The top electrodes were post-annealed in-situ at 600 °C under pO$_2$= 200mbar for 2hours. The top electrodes were then cooled down to room temperature at a rate of 3°C.min$^{-1}$. The magnetization of these films was also measured. The dielectric measurements of the films were performed using a LCR Meter (see chapter 2). Temperature dependence of the capacitance and dielectric loss were recorded upon cooling, from 250K to 5K, as a function of frequency in the 40Hz-1MHz range. Measurements under applied magnetic field were performed under a maximum applied field of 6 Tesla.

5.4 Structure of the films grown on Nb-SrTiO$_3$

Figure 5.2 (a) shows the morphology images of the 40nm TbMnO$_3$ thin film grown on Nb-SrTiO$_3$. The steps of the substrate are not clearly visible, but the Fourier transform of the 5x5µm$^2$ image shows the periodicity of the steps (see right-top inset). The RMS roughness is estimated to be 1.1nm, comparable to that of the 40nm film grown on insulating SrTiO$_3$ under the same conditions. Figure 5.2 (b) shows the XRD pattern of the films, in which no signs of impurity or secondary phases are present. An out-of-plane lattice parameter of c=3.717Å was determined, which is smaller than that of the samples grown under the same oxygen pressure on an undoped substrate (c=3.726
5.4. Structure of the films grown on Nb-SrTiO₃

Figure 5.2: (a) AFM picture for a 40nm TbMnO₃ film on Nb-(001)SrTiO₃. The inset in the left corner shows the AFM images at a smaller scale. The inset on the right corner shows the FFT of the image. (b) 2θ-ω diffractogram showing the epitaxy of the films. The stars correspond to the 40nm film whereas the circles correspond to the 90nm film. (c) Orthorhombic lattice parameter of the films grown on Nb-STO as compared with those of the films grown on an undoped substrate. Horizontal lines signal the bulk values. (d) Blow-up of (b) around the (002) reflection of SrTiO₃. The same symbols as in (b) are used.

Å). This may be due to the very different electronic characteristics of the 2 substrates (SrTiO₃ is an insulator whereas Nb-SrTiO₃ is a n-type semiconductor). Figure 5.2 (c) shows the lattice parameters of the films compared with those of the other films grown at 0.9mbar on SrTiO₃, as determined by reciprocal space mappings around the (103) and (113) of the substrate. Figure 5.2 (d) shows that the 90nm film reflection consists of two peaks, corresponding to the relaxed and strained parts.

The films grown on Nb-SrTiO₃ showed the same general magnetic features as the other samples, namely dominant antiferromagnetic interactions with an induced mag-
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Figure 5.3: Zero-field-cooled (full symbol) and field-cooled (open symbol) of the magnetic moment as a function of temperature for a 90nm TbMnO$_3$ film grown on Nb-SrTiO$_3$.

The magnetic moment, as shown in figure 5.3 (the value of the splitting is included in figure 4.10.)

5.5 Results and discussion

5.5.1 Dielectric behaviour

Figures 5.4 show the evolution of the real and imaginary parts of the dielectric constant as a function of temperature for a 40nm (left panel) and a 90nm (right panel) thick films, respectively, for different frequencies, ranging from 100Hz to 1MHz. As explained before, the 90nm film consists of a strained part and a bulk-like relaxed part (see figure 5.2 (c)-(d)).

Both thicknesses show similar behaviour with temperature: A step-like increase of the dielectric constant at $T \geq 100$K, for frequencies below 100kHz, associated to a peak in the dielectric loss. However, the 90nm film shows a small anomaly in the dielectric constant at the bulk ferroelectric ordering temperature, consistent with the recovery of the cycloidal state in the bulk-like part of the films (figure 5.5 (b)). The anomaly cannot
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Figure 5.4: Left panel: Temperature dependence of the real (a) and imaginary (b) parts of the dielectric constant under different frequencies of the applied voltage for a 40nm TbMnO$_3$ film grown on Nb-doped SrTiO$_3$ substrate. Right panel: Temperature dependence of the real (c) and imaginary (d) parts of the dielectric constant under different frequencies of the applied voltage for a 90nm TbMnO$_3$ film grown on Nb-doped SrTiO$_3$ substrate.

be seen in the 40nm film (figure 5.5 (a)), indicating that the macroscopic ferroelectric state in TbMnO$_3$ is suppressed in the strained films. Above a frequency of 100kHz, the real and imaginary parts of the dielectric constant show very little variations with temperature.

For both thicknesses, the room temperature dielectric constant is as high as 500-1000. In the 40nm film, the low frequency dielectric constant at low temperatures (measured with the field along c), is about 30 [145], which agrees well with the bulk values [28, 54, 146]. The smaller value of the 90nm film is consistent with a two-layer model (strained and relaxed layers), or two capacitors in series for which the total capacitance is smaller than the individual capacitances. At room temperature, the dielectric constant is higher for the 90nm than for the 40nm film. This can be attributed
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Figure 5.5: Low temperature region of figure 5.4, of the real part of the complex dielectric constant for the 40nm (a) and 90nm (b) TbMnO$_3$ film for different frequencies, ranging from 100Hz to 1Mhz. The straight lines are a guide to the eyes.

Figure 5.6 shows the frequency dependence of the real and imaginary part of the complex dielectric constant and the ac conductivity at various temperatures ranging from 10K to 255K for both the 40nm (left panels) and the 90nm films (right panels). In the 40 nm film, two different relaxations are clearly observed for all temperatures. The dielectric constant shows an step-like decrease at about $10^5$ Hz, associated with a peak in the imaginary part (figure 5.6 (a) and (b)). Above 40K, an indication of a second low-frequency relaxation is seen as an increase of the real part and an incipient peak in the imaginary part of the dielectric constant. For the 90nm film, the two mechanisms can also be inferred: the high frequency peak is shifted to higher frequencies and only a tail can be seen in the imaginary part, due to our limited frequency range (figure 5.6 (b), right panel). The relaxation at low frequencies can be observed only at the highest temperatures, and it shifts to lower frequencies, out of our measurable range, for temperatures lower than 175K.

This frequency dispersion is also observed in bulk samples [50, 146] and is discussed in terms of polaron hopping (dynamical localized charge carriers) [35, 50]. Indeed, in the presence of the Jahn-Teller effect, as soon as an electron hops into an
empty $e_g$ orbital, a distortion of the oxygen octahedral cage lowers the symmetry and further splits the $e_g$ and $t_{2g}$ levels. The electron is then more tightly bound, forming a so-called lattice polaron. Similar mechanism is reported for the conduction in other bulk rare earth manganites (orthorhombic or hexagonal) [28, 147, 148]. As it will be described below, our low frequency data is also consistent with polaron hopping.

With respect to the high frequency relaxation, a very recent work from Tokura's group found a similar peak in the dielectric loss for DyMnO$_3$ [149]. The onset of a
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**Figure 5.7:** Frequency dependence of the real and imaginary part of the complex dielectric constant as a function of frequency at a temperature of 10K (a) and 255K (b), for a 40nm $\text{TbMnO}_3$. The grey lines are the fit to the data using a Debye model. (c) Frequency dependence of the real and imaginary part of the complex dielectric constant at 120K.

Peak in the dielectric loss can also be detected in the work of Adem et al. on undoped $\text{TbMnO}_3$, although not discussed [28]. Kagawa et al. [149] have attributed the peak to relaxation of domain walls between domains presenting bc spin cycloids and those of the ac spin cycloids [149]. In the bulk $\text{DyMnO}_3$ compound, the frequency at which the relaxation appears is reported to be $10^7\text{Hz}$ [149], two orders of magnitude higher than that observed for the 40nm film but closer to the frequency suggested by the tail in the imaginary part for the 90nm film. This indicates that the clamping effect from the substrate decreases the relaxation frequency of the domain walls.

By fitting the data at different temperatures, the activations energies associated with the relaxations could be calculated using the relationship $\tau = \tau_0 \exp(E_a/kT)$, where
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Figure 5.8: $1/\tau$ versus temperature, for the high frequency relaxation of the 40nm film, demonstrating the absence of Arrhenius behaviour. The fit to the data are shown as a line.

$E_a$ is the activation energy, $k$ is the Boltzmann constant and $\tau_o$ is the Arrhenius pre-factor. The relaxation time ($\tau$) was taken as the inverse of the frequency at the maximum of the imaginary permittivity. Figure 5.7 shows the frequency dependence of the real part and imaginary part of the dielectric permittivity at a temperature of 10K (a) and 255K (b) for the 40nm film. The lines, which are the fit to the data using a Debye model with a single relaxation time (see Chapter), show that the high frequency region could be well fitted with a relaxation time of the order of $10^{-5}$s at 10K and of the order of $10^{-4}$s at 255K. The intermediate region of temperatures shows the coexistence of the two relaxation mechanisms (see figure 5.7 (c)).

Concerning the high-frequency part, figure 5.8 shows the inverse of the relaxation time as a function of temperature. A weak temperature dependence and non-Arrhenius behaviour is found. At low temperatures, a linear increase with increasing temperature can be seen. However, above $\sim 25$K the behaviour departs from linearity. So, even though the sinusoidal-to-cycloid transition is not observed in the magnetization data, the signature of this transition seems to appear in the dielectric data, affecting the behaviour of the domain wall relaxation. We can then suggest, consistently with our
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Figure 5.9: In ($\tau$) vs. 1/T demonstrating the Arrhenius behaviour for the low frequency relaxation associated to the 40nm film (a) and the 90nm (b). The fits to the data are shown as lines in each case.

findings in Chapter 4, that although long-range order (and, therefore, also ferroelectricity) is precluded by the presence of domain walls, the cycloid structure may be present in the domains at the local scale.

Figure 5.9 shows the Arrhenius plot for the low frequency relaxation in the 40nm (a) and the 90nm (b) films. From the slope of the fits, the activation energy of 0.18eV ($\tau_o=2.45\times10^{-11}$s) was obtained for the low frequency relaxation, for the 40nm film. For the 90nm film, an activation energy of 0.31eV ($\tau_o=9.59\times10^{-12}$s) could be obtained from the data. The values are comparable to those of single crystals of TbMnO$_3$ (0.269eV) and for Tb$_{1-x}$Ca$_x$MnO$_3$, with x=0.1 (0.107eV) [28]. For other manganites, these are found to be 0.215eV (LaMnO$_3$), 0.245eV (NdMnO$_3$) and 0.373eV (HoMnO$_3$) [147], and have been attributed to polaron hopping, as discussed above. Interestingly, these activation energies in manganites have been related to the degree of Jahn-Teller distortion and show an increase with increasing Jahn-Teller distortion [147]. This suggests that the degree of Jahn-Teller distortion is reduced in thin films of TbMnO$_3$, in agreement with a less distorted crystal lattice.

Ionic conduction should also be considered as a plausible mechanism for the low frequency relaxation. In the case of perovskites, in which no interstitial sites are available for hopping of ions, the ionic conduction would likely be due to oxygen vacancies.
However, the activation energy of oxygen diffusion is found to be around 1-1.1 eV [150], suggesting that the activation energies found in the films cannot be attributed to ionic conduction.

Dielectrics having localized charge carriers show an ac conductivity, following the equation \( \sigma = \sigma_{dc} + \sigma_0 \omega^n \), where \( \omega \) is the angular frequency, \( \sigma_0 \) and \( n \) being temperature dependent constants and \( n \) ranging between 0.6 and 1 (there are exceptions of materials having a \( n \) exponent much lower than 0.6 or higher than [96, 151, 152]). By plotting \( \log (\sigma) \) versus \( \log (\omega) \), a dielectric following the "Jonscher's power law" (or the so-called universal dielectric response) shows then a linear behaviour, from whose fit the \( n \) exponent can be obtained. As shown in figure 5.6 (c), this is the case in a wide range of frequencies for the 40nm film (left panels) and the 90nm film (right panels) grown at 0.9 mbar. This is clearer in the 90nm film due to the absence of the high frequency relaxation mechanism in the measured range of temperatures and frequencies. Similar results for the low frequency mechanism have also been reported in single crystals [28] and ceramics [153] of TbMnO\(_3\). The \( n \) exponent obtained from these data vary between 0.4 and 1 (see also chapter 6).

### 5.5.2 Impedance analysis

An impedance analysis was performed, for the first time, for thin films of TbMnO\(_3\). Figure 5.10 shows the evolution of \( \varepsilon'' \) vs \( \varepsilon' \) at different temperatures ranging from 10K to 255K for the 40nm film (a) and 90nm (b). By comparing the plots at 10K and 255K, and as suspected by the fits of the real part and imaginary part of the dielectric constants, both temperatures display a semi-circle, typical for a Debye-like relaxation associated to a model of capacitance and a resistance in series. For the 90nm films, only one semi-circle is obtained for the measured range. For this sample, the high asymmetry of the circles can be attributed to a Debye exponent different that one (see chapter 1), indicating a spread of the relaxation times, due to the presence of a larger amount of disorder in the thicker films. However, the intermediate range of temperature shows
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Figure 5.10: $\varepsilon''$ vs $\varepsilon'$ at different temperatures ranging from 10K to 255K for a 40nm (a) and a 90nm (b) TbMnO$_3$ film

Figure 5.11: Cole-cole plot for the 40nm TbMnO$_3$ film, taken at 109K, where the low and high frequencies relaxations can be clearly seen.

the coexistence of the two relaxations (see figure 5.11) for the 40nm film. As the temperature is decreased, the second semi-circle starts being revealed.

Then, the high dielectric constant observed at room temperature and low frequencies, found to be in the order of 500 for the 40nm film, could be due to the confinement of polarons at the domain walls, causing a kind of depletion layer at the walls or due to the depletion layers at the electrodes/film interfaces (Schottky barrier). In figure 5.12, the frequency dependence of the dielectric constant is plotted for different amplitude of the ac field for a 40nm TbMnO$_3$ film. A clear voltage dependence of the real part of the dielectric constant can be seen, at low frequencies, consistent with the presence...
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Indeed, the ac behaviour of a Schottky contact is dependent on the depletion width for a given voltage [154]. The depletion width can be expressed as \[ W = \sqrt{\frac{2\varepsilon_s (V_{bi} - V_A)}{qN}} \], where \( V_{bi} \) is the built-in voltage in the Schottky contact, \( V_A \) is the applied voltage and \( \varepsilon_s \) is the permittivity of the semiconductor. In turn, the capacitance of the junction (\( C_j \)) can then obtained by \( \varepsilon_s / W \) and it follows that the depletion width being dependent on the applied bias, the capacitance of the junction will be modified and thus will be the permittivity of the sample.

5.5.3 Magnetoelectric properties of the TbMnO\textsubscript{3} films.

Figure 5.13 shows the temperature dependence of the real part of the dielectric constant as a function of temperature under different applied magnetic fields ranging from 0Oe to 60kOe, and measured at 1kHz for the 90nm film.
Figure 5.13: Temperature dependence of the real part of the dielectric constant under different applied magnetic field, from 0 kOe to 60kOe, measured at 1kHz for the 90nm film. The inset shows a zoom around the ferroelectric transition temperature.

From the graph, no influence of the applied field on the behaviour of the real part of the dielectric constant can be observed up to 80K, where the behaviour of the curves under applied magnetic fields starts differing from that of the curved measured without applied field. This can be attributed to the effect of the applied magnetic field on the polaron hopping. The temperature of the ferroelectric anomaly is lower than the one depicted in figure 5.5, but this may be explained by the use of different set-ups and heating rates. The inset of figure 5.13 shows a blow-up around the ferroelectric transition. The amplitude of the anomaly, related to the onset of local ferroelectricity, is not affected by magnetic fields up to 60 kOe. A small increase of the real part of the dielectric constant with increasing magnetic field can be seen. The temperature of the transition is not affected by fields up to 30kOe, but is shifted to lower temperature under an applied field of 60 kOe. This suggests that high enough magnetic fields tend to preclude the onset of ferroelectricity in the films.

A frequency dependence of the dielectric constant for different field and temper-
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Figure 5.14: (a): Resistance versus applied magnetic field for a 90nm TbMnO$_3$ thin film grown at 0.9mbar at different frequencies. (b): Capacitance versus applied magnetic field under different frequencies for a 90nm TbMnO$_3$ thin film grown at 0.9mbar. The data were taken at 5K temperatures was performed. Figure 5.14 shows the magnetoresistance (a) and magnetocapacitance (b) measurements for the 90nm film, as a function of frequency, ranging from 100Hz to 1MHz, measured at 5K, to reduce the influence high temperature relaxation. It can be seen that the magnetocapacitance is a small effect in the film and it is significant only for frequencies above 100kHz, with a magnetocapacitance effect of only 1.6%. However, the magnetoresistance effect is much larger: A small negative magnetoresistance of -20% for an applied field of 20 kOe can be observed at a frequency of 100Hz. By increasing the frequency to 1kHz, no magnetoresistance effect can be seen at any applied magnetic field. By further increasing the frequency, a positive magnetoresistance effect of more than 100% can be observed. The magnetoresistance and magnetocapacitance effects seem to saturate for frequencies above a couple of 100kHz, when the relaxation, attributed to the domain walls starts occurring.

One has to be careful with the interpretation of magnetic field dependence of the dielectric properties. Catalan showed that a magnetocapacitance effect can be observed without a magnetoelectric coupling, due to heterogeneity in the material (Maxwell-Wagner effect) [144]. The magnetocapacitance can be due to colossal magnetoresistance at interfaces (between grains or at domain walls, for example). In the case of
Table 5.1: Core-dominated (CD) and interface-dominated (ID) magnetocapacitance (MC) corresponding to the sign of magnetoresistance (MR) effect as a function of their signs.

<table>
<thead>
<tr>
<th>MR+</th>
<th>MR-</th>
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<tbody>
<tr>
<td>MC+</td>
<td>ID</td>
</tr>
<tr>
<td>MC-</td>
<td>CD</td>
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a core-dominated negative magnetoresistance, a positive sign of the magnetocapacitance should be observed, whereas an interface-dominated negative magnetoresistance effect is expected to induce a negative magnetocapacitance [144]. The opposite should be true for a positive magnetoresistance (see table 5.1).

In our data, a positive magnetoresistance effect is observed over a wide range of frequencies, associated to a positive magnetocapacitance, indicating an interface dominated magnetoresistance. The most likely candidates are the grain boundaries and/or the presence of domain walls.

As discussed above, with decreasing frequency, the magnetoresistance decreases and becomes negative for frequencies below 1kHz, but is still associated with a positive magnetocapacitance, suggesting an core-mediated negative magnetoresistance (see table 5.1). That could arise from the effect of the magnetic field on the polaron hopping. The magnetoresistance and the magnetocapacitance of the 90nm film was measured under different temperatures under a frequency of 1kHz, as shown in figure 5.15 (a) and (b). Under those conditions, the contribution to the magnetocapacitance from the relaxation of the domain walls is minimized to emphasize the core mechanism. The small positive magnetocapacitance (see figure 5.14) decreases with increasing temperature and becomes negative around the ferroelectric transition temperature (T_f 25K). This is still associated to a positive magnetoresistance. From table 5.1, this implies that the magnetoresistance is core-dominated. The change of sign of the magnetocapacitance from positive to negative as also been observed in TbMnO_3 with 2% calcium doping on the rare-earth site, at the ferroelectric transition of 20.5K [146].

In short, in TbMnO_3 thin films, a strong influence of domain walls on the dielec-
5.6 Conclusions

A detailed analysis of the dielectric permittivity in the films has allowed the distinction between the different contributions to the dielectric constant. In the strained films, the low frequency dielectric constant at low temperatures is found to be $\sim 30$ at low temperatures, similar to the reported bulk value. This suggests that, despite the absence of long-range ferroelectricity (which would show as an anomaly in the dielectric constant at $\approx 25\text{K}$), the strained films seem to consist of polar domains, with polarization at the local scale. The main extrinsic contribution to the low frequency response can be attributed to polaron hopping probably induced by charges in depletion layers at the different interfaces present in the films.

The domain walls largely contribute to the dielectric constant and relax at about

![Figure 5.15](image_url) **Figure 5.15:** Magnetoresistance (a) and magnetocapacitance (b) dependence under applied magnetic field up to 10 kOe, measured at different temperature from 25K to 70K under an applied frequency of 1kHz.

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10^5-10^6 Hz. The relaxation of domain walls is shifted to higher frequencies in the case of the partially-relaxed film. This is most likely due to a release of the clamping effect of the substrate. Moreover, the domain relaxation mechanism does not follow an Arrhenius law. However, the inverse of the relaxation times follows a linear behaviour versus temperature up to around 25K, where the behaviour departs from the linear one, suggesting the presence of the sinusoidal to cycloid transition in the films (at the local scale) and consistent with the presence of ferroelectricity. The 90nm film shows a small magnetocapacitance effect of 1%, whereas a magnetoresistance effect as high as 150% could be measured under an applied field of 60 kOe along the in-plane direction, at 5K, at frequencies at which the relaxation of domain wall starts appearing. Under such an applied field, we find that the ferroelectric transition is shifted to slightly lower temperatures, confirming an intrinsic magnetoelectric coupling, even if the effect is small.