DYNAMICS OF COUPLED DEGREES OF FREEDOM
IN MULTIFERROIC TbMnO$_3$

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presented by

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Abstract

This thesis describes three experiments investigating complex dynamic couplings between different degrees of freedom in orthorhombic TbMnO$_3$. TbMnO$_3$ is a perovskite rare-earth manganite exhibiting strong magnetic frustration due to a significant GdFeO$_3$-type distortion. The Mn spins subsystem is paramagnetic at high temperatures. On cooling below 42 K it undergoes a transition to a spin-density-wave state, and at 27 K it makes a transition to a multiferroic state, where a cycloid magnetic order sets in as a result of the interplay between the nearest-neighbor and next-nearest-neighbor superexchanges. The cycloid spin ordering creates a spontaneous ferroelectric polarization along the $c$-axis due to the relativistic inverse Dzyaloshinskii–Moriya interaction, further stabilized by the atomic displacements. This makes the two orders intrinsically related via a strong magnetoelectric coupling. A consequence of this coupling is that in this material there exist additional coupled phonon-magnon excitations termed electromagnons, in which the electric field of light induces the motion of the spins.

The dynamics of coupled degrees of freedom are tracked using a pump-probe technique. The experiments are performed using ultrashort x-ray, optical and THz pulses, taking advantage of capabilities of modern ultrafast lasers and novel sources of x-ray radiation such as x-ray free electron lasers.

The first experiment relates the dynamics of magnetic system of TbMnO$_3$ when excited with the electric field of the incident THz pulse resonant with the electromagnon. The motion of the Mn spins was determined directly during the excitation process by measuring the first harmonic magnetic diffraction peak with femtosecond time resolution. The amplitude of the spin motion was quantified by comparison with the static measurement of the same diffraction peak. The measurement shows that large-amplitude coherent changes in the magnetic structure can be induced on picosecond timescale, several orders of magnitude faster than previously observed. Additionally, the observed amplitude of the coherent excitation shows that ultrafast, heatless domain reorientation using moderately higher THz field strengths should be achievable.

The second experiment looks at the dynamics of the magnetic subsystem after excitation with the optical light resonant with the $d$–$d$ transitions in the material. This excitation creates a population of small polarons via a local release of Jahn–Teller distortion, which couple electronic, lattice and spin degrees of freedom. A relatively slow demagnetization process is observed using time-resolved resonant soft x-ray scattering. The use of different scattering geometries helps to visualize the ultrafast melting process of magnetic subsystem and corresponding orbital deformations. It is found that the pump fluence required to destroy correlations with spin components along the $b$-axis is higher than that required to destroy the correlations with spin components along the $c$-axis which exist only in the multiferroic phase. Additionally, the demagnetization timescale is slower for the Fourier components of magnetic structure along the $b$-axis. This is con-
sistent with the theoretical predictions that the $b$-axis correlations are generally stronger in the orthorhombic manganites across the entire phase diagram. It supports the scenario where the multiferroic phase transition does not separate two competing magnetic orders, but instead the spin-cycloid order builds on top of the pre-existing SDW-like correlations.

The third experiment complements the results obtained in the second experiment by looking at the dynamics of optical reflectivity in the region covering the $d$–$d$ transitions, sensitive to magnetic ordering. Complex spectral dynamics suggest that the $p$–$d$ and $d$–$d$ absorption features react strongly to the underlying magnetic and lattice reordering. Formation of polarons is accompanied by generation of coherent phonons related to the release of the Jahn–Teller distortion. Probing the amplitude of the phonons with different photon energies reveals their strong coupling to the $d$–$d$ transition gap.

The thesis is organized as follows. Chapter 1–3 give theoretical overview of the physics of manganites, multiferroics and particular properties of TbMnO$_3$. Chapter 4 describes the experimental methods. Chapter 5 describes the THz pump–soft x-ray probe experiment where the THz pulse resonantly excites the electromagnon. Chapter 6 relates the time-resolved measurements on different magnetic satellites in a 1.55 eV pump–soft x-ray probe experiment. Chapter 7 describes the 1.55 eV pump–broadband reflectivity probe experiment looking at the transformations of the optical properties of TbMnO$_3$ in the range covered by the spin-sensitive $d$–$d$ and $p$–$d$ excitations. Finally, the appendices give an extensive overview on the data analysis methods.
Kurzfassung


Beim zweiten Experiment wird die Antwort des magnetischen Systems auf Anregung der optische d–d-Übergänge untersucht. Diese Anregung erzeugt durch lokale Relaxierung der Jahn-Teller-Verzerrung eine Population kleiner Polaronen, welche Gitter-, Spin- und elektronische Freiheitsgrade verbinden. Mit Hilfe zeitaufgelöster resonanter Beugungsversuche mit weichen Röntgenstrahlen beobachtet man eine relativ langsame
Demagnetisierung. Die Kombination verschiedener Streugeometrien erlaubt die Visualisierung des Demagnetisierungsvorgangs und der einhergehenden Deformationen der elektronischen Orbitale. Messungen bei verschiedenen Pump-Fluenzen zeigen, dass die Korrelationen der Spinmomente entlang der $b$-Achse (SDW) robuster sind als die einfacher zu zerstörenden Korrelationen entlang der $c$-Achse (Zykloide), welche nur im multiferroischen Zustand existieren. Auch ist die Demagnetisierung für die Fourierkomponenten der magnetischen Struktur entlang der $b$-Achse langsamer. All dies ist konsistent mit den theoretischen Vorhersagen, dass die Korrelationen entlang der $b$-Achse in orthorhombischen Manganiten generell, im gesamten Phasendiagramm, stärker sind. Die Messungen unterstützen das Szenario, in dem der Übergang zur multiferroischen Phase nicht zwei konkurrierende magnetische Ordnungen trennt, sondern die zykloidale Ordnung auf der schon existierenden, SDW-artigen Ordnung aufbaut.


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Introduction

With the technological advances in the last several years, science has become equipped with a new tool, allowing to investigate the properties of materials in a time domain. While majority of scientific measurements are performed in the conditions of thermodynamic equilibrium between the sample and applied external parameters, the time-resolved experiments operate on a different principle. The sample is impulsively disturbed out of equilibrium in a selective and non-adiabatic fashion, and the experimenter tracks the energy flow between different degrees of freedom of the material by means of pulsed probe of particular observables. Great advantage of this method is that it allows to reach to the phases and properties of materials not accessible with the adiabatic experiments, and offers a unique way to investigate static and dynamic coupling between the subsystems of a sample, and ultimate timescales of the phenomena. Additionally, it offers a way to control and manipulate the properties of materials on the ultrafast timescale in a coherent way, as the excitation happens in a selective fashion, and by appropriate tayloring of the incident pump pulse, the energy can be transferred very efficiently to a particular degree of freedom.

In the experiments discussed in this thesis, novel sources of femtosecond pulses of electromagnetic radiation were employed. Recent technological advances allow for generation of ultrashort pulses in a much broader spectrum of electromagnetic radiation than just the optical light, spanning the range from THz (far-IR, \(\sim 1\) meV) to soft and hard x-rays (\(\sim 0.5\)–10 keV). The THz physics is undergoing an extremely fast development due to overcoming the THz gap, and this frequency regime offers an insight into the previously hardly accessible part of the spectrum containing soft modes and other low frequency excitations. Technique of magnetic resonant soft x-ray scattering, developed not long ago in the static case and available as a time-resolved probe only in last years, offers a unique possibility of direct visualization of magnetic order dynamics in materials.

The technological advances are superimposed with the on-going renaissance of the multiferroics, materials exhibiting more than one ferroic order. Multiferroics offer new routes for domain control, and exhibit rich underlying physics, concerning among others incommensurate ordering, frustrated magnetic phenomena and unusual degrees of freedom.
The thesis addresses the topic of ultrafast dynamics of multiferroics, which has not yet received the same attention as the static studies of these materials. It concentrates on orthorhombic TbMnO$_3$, a model representative of the family of spin-cycloid multiferroics, where the ferroelectric polarization is a driven by relativistic interactions between the non-collinearly ordered spins.

The referred experiments look into different disturbances to the magnetic order of TbMnO$_3$, which may possibly lead to achieving ultrafast control over its domain state. The experiments investigate the timescales associated with different ways to transiently alter the magnetic order. The use of probes sensitive to different degrees of freedom allows for tracking the couplings between the subsystems and investigation of the relationship between lattice, electronic, spin and orbital degrees of freedom. The experimental results are supported with a theoretical section discussing the physics of multiferroic manganites, and a description of experimental methods. As taking a measurement more and more often means a necessity to process large amount of data, an extensive overview of used data analysis methods is given as a supplement.
Chapter 1

Properties of perovskite manganites

1.1 Introduction

Rare earth manganites of chemical formula $R$MnO$_3$ are a perfect playground for investigating emergent phenomena in magnetically frustrated systems [1, 2]. This is because on one hand they are characterized by relatively simple crystallographic structure, and on the other hand, many intriguing magnetic phases can be reached on the phase diagram just by slight modification of the structure or doping. The valence of the rare-earth ion determines the valence of the Mn ion and in turn leads to rise of intriguing magnetic phases, as seen in $(\text{Pr},\text{Ca},\text{La},\text{Sr})$MnO$_3$ solid solutions.

Because of their rich physics, single and mixed-valence manganites have been rewarding samples to measure in different kinds of ultrafast pump–probe experiments [3–10]. For example, it has been shown that a mid-IR laser pulse resonant with a phonon can induce a metal-insulator transition [3], and a population of coherent modes related to the lattice and orbital order is generated after the optical excitation [4, 8–10]. Manganites were also the materials used to show that a single order parameter may describe all the triggered dynamics [4], and in a demonstration of the mechanism of indirect driving a Raman mode via lattice anharmonicities [7].

In order to understand the results of the experiments with the sample disturbed strongly out of equilibrium, it is essential to know their properties in the static case. The experiment referred in this thesis concern only one member of the $R$MnO$_3$ manganite family, TbMnO$_3$. Many details of the microscopic physics of this crystal can be learned by looking at the whole family of stoichiometric orthorhombic $R$MnO$_3$ manganites, where $R = \text{La} \ldots \text{Yb}$. They are isostructural and much can be learned though by analyzing how the physics of $R$MnO$_3$ place at the background of the properties of its sister compounds. TbMnO$_3$ is a single-valent manganite and so the discussion will concern
1.2 Lattice and electronic structure

$\text{R MnO}_3$ where rare-earth has a configuration $R^{3+}$. In case of such manganites, it turns out that the main phenomena driving the formation of 3$d$ magnetic order are related to the radius of the $R$-ion and thus the degree of lattice distortion. The phase diagram of pure $\text{R MnO}_3$ can be to big extent reproduced by solid solutions of (Eu,Y,Lu)MnO$_3$, and most experimental findings obtained for a mixed crystal exhibiting the same magnetic phase are also valid for a pure compound being its counterpart [11].

This chapter gives an overview of the most important phenomena in single valent $\text{R MnO}_3$, with focus on the particular aspects helpful for understanding the physics of TbMnO$_3$. It discusses the structural and electronic aspects, magnetic phase diagram as well as Raman and optical spectra, the knowledge of which leads to better understanding of the experiments on TbMnO$_3$.

1.2 Lattice and electronic structure

Most of the physics of the manganites can be captured within the Mott–Hubbard picture [12]. The manganese ions with Mn$^{3+}$ ($d^4$) configuration are characterized by reasonably well localized electrons and spins. The hopping of electrons between the Mn sites is possible because of intermediate action of the hybridization with $p$-orbitals of the oxygen ligand, forming the Mn–O–Mn bond.

1.2.1 Geometrical considerations

In ideal perovskite of the $\text{ABO}_3$ formula, the $B$ atom is surrounded by six oxygen ions according to the cubic symmetry, and so the oxygens form an ideal octahedron around it. The $A$ atom—here it would be the rare-earth ion—is placed in the corners of the cubic unit cell, equidistant to the oxygens. In case of manganites, $B$ is a magnetic Mn ion with $d$-electrons. Real $\text{R MnO}_3$ do not crystallize as ideal perovskites, because they suffer from a strong mismatch between the ionic radius of the rare earth ion and the volume of the void between the MnO$_6$ octahedra. This can be quantified using a geometrical tolerance factor:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)},$$

where $R_A$, $R_B$, $R_O$ are the ionic radii of A, B and O ions. The $R = \text{La…Yb}$ series has $t$ values of $0.88 \ldots 0.97$, with $t \approx 0.90$ for TbMnO$_3$.

To compensate for the strain created by this mismatch of the ionic sizes, the structure distorts: the octahedra rotate along the high-symmetric axes, and this effect is accompanied by some degree of distortion of the octahedra (Fig. 1.1). Since every oxygen atom forms an apex of two octahedra, the rotations form in the lattice in a cooperative way. In case of $\text{R MnO}_3$, the octahedra rotate collectively about the cubic [110] and [001] (orthorhombic [010] and [001]) directions [12]. Such a distortion results
with tilting the Mn–O–Mn bond from the optimal $180^\circ$ angle towards smaller angles on the order of $150^\circ$. Following the notation of Glazer [13], this pattern corresponds to $a^-b^+a^-$: antiphase rotation about $a$ axis, in-phase rotation along the $b$ axis with different amplitude, and anti-phase rotation about the $c$ axis, with the same amplitude as along $a$ (where the phase relation of the rotation is evaluated between the neighboring manganese sites). It is named conventionally a GdFeO$_3$ or CaTiO$_3$ distortion.

Crystallographically, it leads to symmetry lowering from the parent $Pm\bar{3}m$ space group to the $Pbnm$ space group ($a < b < c$). The new orthorhombic $a$, $b$ crystal axes are oriented diagonally between the $a$, $b$ axes of parent cubic coordinate system with the length approximately $\sqrt{2}$ bigger, and the $c$ axis length becomes doubled with the same direction in space.

1.2.2 Jahn–Teller effect

In the pure $RMnO_3$ with the rare-earth ions having the $R^{3+}$ electronic configuration, the manganese ion has an $Mn^{3+}$ configuration, which corresponds to the $d^4$ setting. In this situation, it is beneficial for the structure to undergo a Jahn–Teller (JT) distortion. The effect of the crystal field and JT mechanism on the energy level structure of the manganese will be discussed here following [12].

In the perovskite manganite crystal, the Mn ion is surrounded by an octahedron consisting of 6 oxygen anions. In case of an ideal perovskite the Mn is subject to crystal field of a cubic symmetry coming from octahedral arrangement of negative point charges around it. The electric field of the ligands modifies the energy levels of the Mn orbitals, splitting five available $d$-levels of the manganese ion into a set of 3 degenerate $t_{2g}$ and 2 degenerate $e_g$ orbitals (Fig. 1.2a).

In case of a $d^4$ manganese, there is additional effect present. The 4 spins of 3$d$ shell of the Mn will occupy the 3 $t_{2g}$ levels and one $e_g$ level following Hund’s rule in a high-spin configuration. In this case the system can lower its energy by spontaneously undergoing further structural distortion from the ideal octahedron within the Jahn–Teller mechanism, which will lift the $t_{2g}$ and $e_g$ degeneracy (Fig. 1.2a). Similarly as with the distortion due to the geometrical effects, in a crystal lattice these distortions happen in a cooperative way, being the source of orbital order.

The JT distortions of the octahedra can be described using modes denoted typically as $Q_2$, $Q_3$, where

$$Q_2 = (x - y)/\sqrt{2},$$
$$Q_3 = (2z - x - y)/\sqrt{6}.$$ 

$Q_2$ corresponds to the elongation along $x$, contraction along $y$ and $z$ untouched, and $Q_3$ to elongation along $z$ and contraction along $x$ and $y$ (see Fig. 1.2). The $x$, $y$, $z$ directions are defined locally for a MnO$_6$ octahedron.
1.2 Lattice and electronic structure

Figure 1.1: GdFeO$_3$ distortion – rotation pattern of the octahedra (the rare-earth ions have been removed for clarity). This and other visualizations of crystal structures were made using [14].

Figure 1.2: (a) Electronic levels of the Mn$^{3+}$ ($d^4$) ion in a cubic and tetragonal crystal field; (b) $Q_2, Q_3$ octahedral distortion modes; (c) energy levels due to the $p-d$ hybridization (“a”: antibonding, “b”: bonding) [12]
Properties of perovskite manganites

Figure 1.3: Orbital mixing angle and its influence on the $e_g$ orbital configuration (a) and the JT distortion (b) [12]. Blue arrow points to the value taken by TbMnO$_3$.

Figure 1.4: Structural parameters for manganites with different R-ions; right: Mn–O–Mn bond angle ($\theta$) and lengths of the Mn–O bonds, left: phase transition temperatures $T_{JT}$ and $T_N$, orbital mixing angle $\phi$ ($\gamma$), magnitudes of $Q_2,Q_3$ distortions, total JT distortion $\rho_0$ [15]. Blue arrow points to the values taken by TbMnO$_3$. 
1.2 Lattice and electronic structure

The degree in which particular JT modes contribute to the overall JT deformation of the octahedron can be quantified by an orbital mixing angle Φ

$$\tan \Phi = \frac{\sqrt{3} (l - s)}{2m - l - s}.$$ 

Here \(l, m, s\) are long, medium and short Mn–O bonds within the local coordinate system of the octahedron corresponding to \(y, z, x\) axes respectively. From \(\Phi\) one can calculate the position of the distortion on the \((Q_2, Q_3)\) space, as illustrated in Fig. 1.3b. Additionally, the same quantity defines the state forming particular \(e_g\) configuration, composed of a superposition of the pure \(|z^2\rangle\)-type and \(|x^2 - y^2\rangle\) type \(e_g\) wavefunctions (Fig. 1.3a).

In the \(R\text{MnO}_3\) family, the size of the \(R\)-ion determines the bond angle \(\theta\) almost linearly, but the relation to the orbital angle is not as straightforward (Fig. 1.4). It seems that the bond-lengths exhibit a mixing-like behavior in the range of ionic radius size of 1.09–1.13 Å, corresponding to the elements in the region of Sm–Tb (Fig. 1.4). Additionally, \(\text{TbMnO}_3\) is in the region where the orbital angle takes the largest value in the whole \(R\text{MnO}_3\) series. For the La and Tb these values of \(\Phi\) in the range of 107–110° and 111–115° respectively (Fig. 1.4). This means that in case of \(\text{TbMnO}_3\), the mixed state is composed predominantly of the \(|y^2\rangle\) state (120°) with some admixture of the \(|x^2 - z^2\rangle\) state. In terms of the octahedral distortion pattern, this corresponds to elongation along \(y\), contraction along \(x\) and a slightly smaller contraction along \(z\). The local \(y, x\) axes alternate in a staggered fashion within the \((ab)\)-plane.

In general, in manganites the JT effect is very strong, which is supported by very high JT ordering temperatures \((T_{JT}\) increases from 750 K for \(\text{LaMnO}_3\) to 1500 K for \(\text{TbMnO}_3\) [15]). The energy of the splitting is estimated to be 1.6–2.2 eV.

1.2.3 \(p–d\) hybridization

The crystal field splitting and JT effect discussed above are not the only phenomena influencing the energies of the orbitals. There is additional effect lifting the initial degeneration of the \(d\) levels, coming from the hybrydization of the \(p\) and \(d\) orbitals between the Mn ion and oxygen ligand (Fig. 1.2c).

The \(p–d\) hybridization leads to the same type of degeneracy lift as the crystal field splitting, and numerically can be even stronger, however it does not provide an as intuitive qualitative understanding as the JT picture.

This phenomenon gives rise to additional hopping processes apart from the basic Mott–Hubbard \(d–d\) excitations, namely \(p–d\) excitations (charge-transfer transitions). In reality, the \(d–d\) processes are also mediated by the \(p\) orbitals. Generally speaking, depending on the relation between the Coulomb \(d–d\) repulsion \(U_{dd}\) and the \(p–d\) energy cost \(\Delta_{CT}\), the lowest charge-carrying excitations may be either \(d–d\)- or \(p–d\)-type, and the crystal may be classified as a Mott insulator or a charge-transfer insulator within...
the Zaanen–Sawatzky–Allen scheme [12]. Detailed analysis of the optical spectra of manganites suggests however that $R\text{MnO}_3$ possess characteristics of both models, since there are both types of excitations present in the same energy range within the optical gap [16]. This will be discussed in Section 1.6.

1.3 Magnetic interactions

In $R\text{MnO}_3$ one can observe different types of magnetic interactions simultaneously, and a delicate balance between them sets the resulting magnetic ordering. Here following [12] we briefly discuss the physical nature of the most important ones.

1.3.1 Exchange interactions

The source of the exchange interaction is the energy gain obtained by partial delocalization of the spins. Within the Mott–Hubbard scenario, the system can decrease its energy when the localized spins become long-range ordered. The delocalization, leading to energy gain, can happen via processes of virtual hopping of the spins between the sites, and these are the strongest when the spins are aligned with respect to each other. This interaction is described as an effective exchange interaction between the neighboring $d$ sites. In the simplest case it is antiferromagnetic, as hopping between the non-degenerate levels is only possible when the spins aligned anti-parallel. However in reality the sign, character and strength of the exchange interaction is affected by geometry of the Mn–O–Mn bond, crystalline symmetry, specific type of orbital occupation of the Mn ion, intermediate ligands.

Phenomenologically, one can determine the sign and approximate strength of the superexchange using the Goodenough–Anderson–Kanamori rules: (1) virtual hopping of the spins between two occupied orbitals either being nearest neighbors or mediated by the ligand demands that the spins are aligned antiparallel, leading to strong antiferromagnetic exchange; (2) if the hopping process would concern a transfer between empty and occupied orbital (or if both occupied orbitals are orthogonal), connected via the same $p$-orbital, the exchange will be weak and ferromagnetic; (3) if both orbitals are occupied, but they overlap with different $p$-orbitals of the ligand, the exchange is weak and ferromagnetic.

In the systems with many competing exchange paths, the exchange interaction between next-nearest-neighbors may become equally important as the nearest-neighbor processes, and a competition between NN and NNN exchanges may lead to rise of frustrated magnetic phases. This is thought to be a microscopic reason of the cycloidal spin ordering in TbMnO$_3$ and will be discussed in more detail in next sections.

While it can lead to profound magnetic phase transition in mixed valence compounds, of less importance in single-valent $R\text{MnO}_3$ is the mechanism of double-exchange. It comes
from the fact that delocalization of electrons from high- to low-valent ions lowers the ki-
netic energy of the system. Since it happens between the empty and occupied orbital, 
Hund’s rule demands that both ions need to have spins aligned parallel. Effectively it is al-
ways a ferromagnetic coupling (although overall it may lead to appearance of interme-
tiate, canted phases as well), but it requires a presence of mobile electrons, for exam-
ple introduced by doping.

1.3.2 Role of spin orbit coupling

Spin-orbit interaction is a relativistic interaction which couples together the spin and or-
bital moments into the total angular momentum. In case of transition metals, it is weak 
enough so that the effective spins and orbital moment couple together only as net values 
of $L$ and $S$, and its value is usually smaller than the crystal-field splitting. The main re-
sult of this interaction is to tie together the orientation of spin and corresponding 
orbital degree of freedom.

Magnetic anisotropy

Spin-orbit coupling is a requirement for pinning the orientation of the magnetic structure 
to the lattice crystallographic directions. When the orientation of the orbitals is set 
by the crystalline field, the spin-orbit interaction couples the orientations of orbitals 
and spins. In case of long-range ordered magnetic order existing in the crystal, this 
mechanism gives rise to an anisotropy of magnetic structure and makes it take a defined 
orientation with respect to the crystal axes.

Microscopically it is expressed by single-site anisotropy and exchange anisotropy. In some 
electronic configurations, the spin-orbit coupling may compete with the Jahn– 
Teller effect causing lattice distortions and magnetoelastic effects.

Dzialoshinskii–Moriya interaction

When the Mn–O–Mn bond loses the center of inversion, for example by decrease of 
the bond angle from 180°, additional antisymmetric interaction becomes active, namely

![Figure 1.5: Schematic illustrating the directions of the vectors involved in the DM in-
teraction (a), as well as the effect of the DM and inverse DM interaction on the spin 
directions and ligand ion displacement respectively (b).]
Dzialoshinskii–Moriya (DM) interaction. Here the spin-orbit coupling is necessary to enable the spins to interact with each other in an antisymmetric fashion. It is a relatively strong interaction (on the order of exchange anisotropy), and is thought to be an important factor in the structures exhibiting cycloidal and spiral ordering, it is also responsible for appearance of weak ferromagnetism in otherwise AFM crystals.

In case of a bent Mn–O–Mn bond with both manganese possessing classical spins, the DM interaction will drag the spin directions so that they become canted with respect to each other. The energy of the interaction is determined by

\[ H_{DM} \propto \mathbf{D} \cdot (S_i \times S_j) \] (1.1)

Here \( \mathbf{D} \propto \mathbf{e}_{ij} \times \Delta x \) is the DM vector, related to the oxygen displacement \( \Delta x \) and with the magnitude determined by the strength of spin-orbit coupling (Fig. 1.5). Because the DM energy is related to a cross product of spins \( S_i, S_j \), the interaction favors their non-collinear arrangement. In case of inverse DM interaction, the origin is a non-collinear spin arrangement and the coupling further deforms the bond.

Additionally, the DM interaction may be accompanied with the creation of a local electric dipole moment on the Mn–O–Mn bond. This is further discussed in Chapter 2 describing how it influences the multiferroicity in spin-cycloidal crystals.

### 1.4 Magnetic phase diagram

As discussed above, there are many components influencing the resulting magnetic state of a particular manganite. The phase diagram for the whole family of \( R = \text{La...Yb} \) is summarized in Fig. 1.6.

As the size of the \( R \) ion becomes smaller, the Mn–O–Mn distortion increases, which influences the strength of exchange constants. The A-type AFM magnetic order—where the spins are ordered AFM along the \( c \)-direction and FM within the \( (ab) \)-plane—becomes less and less stable (accompanied with the decrease of Néel temperature \( T_N \)).

On some point the A-AFM phase becomes less stable than other magnetic phases, and a crystal enters a region of strong magnetic frustrations, where the ground state can be a spin-density-wave (SDW) or spin-cycloidal phase. These phases are also ordered AFM along the \( c \)-axis and FM along the \( a \)-axis, however along \( b \) they become incommensurately modulated. The SDW phase is collinear and the density of the \( b \)-oriented spin varies sinusoidally along \( b \). The cycloidal phase consist of an elliptical cycloid within the \( (bc) \)-plane, coupled AFM along \( c \) and FM along \( a \).

Moving further on the phase diagram, for very small rare earth ions the ground state becomes stabilized in the E-type AFM order, where the spins follow an up-up-down-down pattern along the cubic axes, coupled AFM along \( c \).

Out of the phases described above, two are multiferroic: the cycloid phase due to the presence of DM-type interaction coupling the canted spin pairs and electric dipole
1.4 Magnetic phase diagram

Figure 1.6: Magnetic phases in stoichiometric \(RMnO_3\) [17]. (a–b) Phase diagram as a function of Mn–O–Mn bond angle and therefore \(R\)-ionic radius, (c–f) schematics describing types of magnetic ordering encountered in particular phases.

Figure 1.7: Properties of pure and solid solutions of \(RMnO_3\) showing that the main driving force behind the particular magnetic phase and corresponding physical properties of the crystal can be assigned to the effective ionic radius of the rare earth [11]. Blue arrow points to the position of TbMnO\(_3\) on the phase diagram.
moment, and the E-type AFM phase, where ferroelectricity arises due to the symmetric exchange striction. The former, exhibited by TbMnO$_3$, will be discussed in detail in Chapters 2–3.

It is understood that presence of the 4$f$-electrons on the rare earth site has very little influence on the magnetic properties of the crystal in the regime above 10 K, below which the 4$f$-electrons acquire their own ordering. This is supported by the fact that the qualitative shape of the phase diagram can be very well reproduced by the mixture of (Eu,Y) on the rare-earth site, chosen to obtain the same average ionic radius as the stoichiometric compounds.

The role of the $R$-ions is still under debate. In principle, the MF phase can be obtained in manganites where $R$-ions do not possess any magnetic moment, such as solid solutions of (Eu,Y)MnO$_3$. However, it is understood that the $f$-spins of the rare-earth ions help in stabilizing the ferroelectric polarization above the temperature of their own ordering by acquiring the same magnetic structure as the manganese spins [18, 19].

It is insightful to look further at the microscopic mechanisms driving the stabilization of particular phases. The effective exchange interactions along $a$, $b$, $c$ directions are the summation of exchange interactions between both $t_{2g}$ and $e_{g}$ orbitals [15]. In principle, between the $t_{2g}$ core spins there exist a three-dimensional AFM interaction. The $e_{g}^{0}$-$e_{g}^{0}$ coupling along $c$ is also AFM, while within the $(ab)$-plane it is FM and dominates the $J_{ab}$. Deep in the range of the A-AFM ordering (La) the magnetic structure can be very well explained by simple competition between these two NN AFM and FM exchanges [22].

For compounds with a smaller radius of the rare-earth ion, the strength of the FM superexchange within the $(ab)$-plane is decreased. It corresponds to a decrease of the effective $J_{ab}$ from 1.67 meV in LaMnO$_3$ to 0.3 meV in TbMnO$_3$ [23]. This is because the total magnitude of the JT distortion increases with decreasing ionic radius, enlarging the effective CT gap as well [15]. Increasing distortion of the Mn–O–Mn angle

Figure 1.8: (a) Exchange paths of the NN and NNN exchange constants in $RMnO_3$ and (b) calculated phase diagram plotted as a function of NNN exchange constant $J_2$ [20, 21]
leads to a decrease in spin hopping efficiency along the bond and therefore decrease of the strength of FM exchange [12].

Meanwhile, the same process leads to increase of importance of the next-nearest neighbor exchange constants, since increased GdFeO$_3$ distortion means that the pairs of oxygen anions come closer to each other, this shortening being around 10% comparing the value for LaMnO$_3$ and TbMnO$_3$ (see Fig. 1.8a for a sketch of the exchange paths) [22].

It turns out that since the onset of the frustration between the NN and NNN superexchange processes, the phase diagram is very strongly (almost solely) determined by the value of the NNN exchange along the $b$-axis, $J_2$, and the sequence of phase transitions across the ionic size can be reproduced very accurately by taking a detailed Heisenberg Hamiltonian of the system and changing the $J_2$ value while keeping all the other exchanges constant (Fig. 1.8) [20, 21]. The compounds for which this process is applicable are $RMnO_3$ in the vicinity of the multiferroic phases (Gd, Tb, Dy, Ho...Yb).

The simplest solution to this frustrated ground state is a state where the spins form a cycloid propagating along a particular direction in the crystal [12]. In the simplest case, the propagation vector can be determined within the mean-field theory by simple minimalization of the magnetic Hamiltonian, and is set by $\cos q = -J_{NN}/4J_{NNN}$. Here $q$ can be incommensurate and can vary in a smooth fashion with changing the ratio of the exchange constants.

### 1.5 Raman spectra

The transition from the parent cubic perovskite to the GdFeO$_3$-distorted structure is accompanied with a lowering of symmetry. As a consequence, additional phonon modes appear in the IR and Raman spectra.

The IR and Raman modes can be classified according to their frequency and ions taking part in the movement within the mode [25–27]. Motions of the $R$, Mn ions

\begin{table}[h]
\centering
\begin{tabular}{c|cccc}
 & $a$ & $b$ & $d$ & $f$ & $h$
\hline
$A_2$ & $B_3$ & $B_1$ & $B_2$ & $B_4$
\hline
$A_1$ & $A_1$ & $A_1$ & $A_1$ & $A_1$
\hline
$A_2$ & $B_3$ & $B_1$ & $B_2$ & $B_4$
\hline

\end{tabular}
\end{table}

Figure 1.9: Explicit forms of the Raman tensors in the $Pbnm$ space group [24]
happen in the range of 3–9 THz, tilting, buckling, rotations of the octahedra—9–15 THz, and stretching, internal modes of the octahedra—15–21 THz.

Additionally, in the multiferroic phases, there exist low frequency, IR- and Raman-active hybrid magnon-phonon modes termed electromagnons, discussed further in Chapter 2.

Since there are no Raman-active modes in the cubic perovskites, all the Raman modes appear due to the GdFeO$_3$ distortions. There are 24 Raman-active modes: 7 $A_g$, 5 $B_{1g}$, 7 $B_{2g}$ and 5 $B_{3g}$ [26]. From symmetry considerations [28] one can identify the forms of the Raman scattering matrices (Fig. 1.9).

Taking into account the direction of propagation of the incident and scattered light, $k_i$ and $k_s$, as well as their polarization $e_i$ and $e_s$ with respect to the crystal axes, one can identify requirements to observe particular Raman phonons [27]. For the propagation of light along the $Pbnm$ b-axis, the following mode symmetries are allowed: $A_g$ for incident and scattered light polarized both along a or c, and $B_{3g}$ for the two polarizations crossed.

Particularly connected to the distortion from the cubic symmetry are the Raman modes $A_g(1)$ and $A_g(4)$ (Fig. 1.10) [30]. The $A_g(1)$ mode is the in-phase stretching of
1.6 Optical spectra

the octahedron, corresponding directly to the Jahn–Teller $Q_2$ mode. The $A_g(4)$ mode is responsible for the antiphase rotation of the MnO$_6$ octahedra about the $b$-axis, which corresponds to one of the modes involved in the GdFeO$_3$ distortion.

Mixing of the Raman phonons

While decreasing the size of the $R$ ion, another effect can be seen concerning the lattice dynamics. It turns out that in the region corresponding to the elements Tb, Gd, Eu, Sm there is a strong mixing of particular Raman phonons—the $A_g(1)$ and $A_g(3)$ modes become very close in frequency and as a result they acquire a strongly mixed character. For the ions far away from this region, such as La on one side and Ho on the other, the modes are well separated, with the higher frequency mode being $A_g(1)$ or $A_g(3)$ respectively. The coupling constant between the two modes has been estimated to $20 \text{ cm}^{-1}$ (2.5 meV) [26]. The mixing is present both at room temperature (paramagnetic phase) and at 10 K (magnetically ordered phases) [29]. The region when the phonon mixing appears, corresponds to the region with the mixing-like behavior of the lengths of the Mn–O bonds and with the strongest admixture of the $Q_3$ mode (cf. Fig. 1.4). The corresponding atomic displacement patterns are depicted in Fig. 1.10—the in-phase stretching ($A_g(1)$), corresponding directly to the Jahn–Teller $Q_2$ mode (cf. Fig. 1.2), and the out-of-phase bending about the cubic [101] axis ($A_g(3)$). This behavior is present both in room temperature and in 10 K [29]. With decreasing of the ionic size, phonon frequencies generally harden, apart from the $A_g(1)$ (JT $Q_2$) mode, which is very little affected.

1.6 Optical spectra

Main features of the optical spectra of $RMnO_3$ can be seen in Fig. 1.11. They consist of two main regions of interest: 1–3 eV and 3–6 eV. The dominant feature in the lower energy range is attributed to the $d$–$d$ transitions, and the higher energy range corresponds to the $p$–$d$ transitions.

$d$–$d$ transitions

The $d$–$d$ transitions consist of the $e_g$ electron hopping between different orbitals of the Mn ion. The spectral weight of this transition has been shown to strongly depend on the orbital mixing angle and the buckling angle of the octahedra [16, 31]. For $RMnO_3$ with $R$ smaller than La the spectral weight decreases with decreasing size of the ion, and the central frequency becomes blueshifted from 2.0 eV to 2.2 eV. This is in agreement with the observation that the JT distortion increases for smaller rare-earth ions and the JT gap becomes bigger.
While initially these transitions were attributed to the on-site transitions between different $e_g$ levels of a Mn ion [32], high spectral weight points to their charge-transfer character. Theoretical considerations identify this transition as a high-spin two-center transition [16, 33].

**p–d transitions**

In a detail, the energy diagram of the MnO$_6$ octahedron is more complicated than depicted in Fig. 1.2 [34], and when the optical transitions are concerned, they can happen between different ligand and manganese levels.

The source of $p–d$ transitions is the transfer of the electron from the 2$p$-orbital of the oxygen ligand onto the empty orbital of manganese. Because the $e_g$ level is split due to the JT splitting, the absorption peaks exhibit a doublet structure. Ordered with raising energy, we can identify features at

- 1.3, 1.9 eV: $t_{1u}(\pi) \rightarrow e_g$ connected to weak nontetragonal distortions of the octahedra
- 2.3, 2.65 eV: $t_{2u}(\pi) \rightarrow e_g$
- 3.0, 3.9 eV: $t_{1u}(\pi) \rightarrow e_g$
- 4.65 eV: $t_{2u}(\pi) \rightarrow t_{2g}$
- 5.3 eV: $t_{1u}(\sigma) \rightarrow e_g$
1.6 Optical spectra

Figure 1.12: Evolution of spectral weight for the transitions within AFM and FM ordered clusters upon crossing the magnetic phase transition [16].

One can see that there is a significant overlap between $p$–$d$ and $d$–$d$ transitions in the region of 1–3 eV, however the $p$–$d$ transitions show up as much weaker and narrower peaks in the optical spectrum.

**Temperature dependence**

The structural variation of the $RMnO_3$ upon changing the temperature is very subtle and so the onset of magnetic correlations plays a role in the evolution of the optical spectrum. The intensity of both $d$–$d$ and $p$–$d$ transitions is shown to depend linearly on the nearest-neighbor spin-spin correlation function $\langle (\hat{S}_1 \cdot \hat{S}_2) \rangle$ [16], which does not disappear completely above $T_N$. Overall, as a function of temperature, in the $d$–$d$ transition region there is a spectral weight transfer between the high-spin and low-spin subbands [33]. Instead of following the square of the sublattice magnetization, the spectral weight of the transitions changes smoothly over the phase transition, reaching the paramagnetic limit high above the transition temperature (Fig. 1.12). In particular, room temperature is not high enough to reach the high-$T$ limit for LaMnO$_3$ ($T_N = 140$ K), but it is enough for the manganites with transition temperatures in the range of 40–50 K.

Both $d$–$d$ and $p$–$d$ transitions are thought to exhibit the same dependence on the spin-spin correlation function [16]. However, for the $d$–$d$ transitions the relative change of the optical properties is much larger upon the magnetic phase transition than for the $p$–$d$ transitions.

**Crystal anisotropy**

The spectral weight of the optical transitions measured with light polarized along a particular crystal axis is strongly connected with the geometry of the lattice, because of underlying anisotropy. On average, taking into account a typical value of the orbital mixing angle (ca. $110^\circ$), the spectral weight of $p$–$d$ transitions $\parallel c$ is 1.5 times bigger than within the $(ab)$-plane. For the $d$–$d$ transitions, this ratio depends not only on the orbital mixing angle, but also on the ratio between kinetic contributions to the $e_g$–$e_g$ exchange integral.
Looking at the anisotropy connected to the spin-spin correlations, the \( d-d \) transitions feel a cost associated with the Hund’s coupling between the excited \( e_g \) spin and a static \( t_{2g} \) spin on a site onto which it jumps. Since the effective magnetic ordering in manganites is different (FM, AFM...) along particular directions or planes, the ratio of spectral weights of the spin contribution to the \( d-d \) transition tends to limit at \( SW_c/SW_{ab} \rightarrow 0 \) in the limit of high temperatures and \( SW_c/SW_{ab} \rightarrow 0 \) in the limit of low temperatures.

1.7 Anti-Jahn–Teller polaron

In the following section we introduce the anti-Jahn–Teller (AJT) polaron, the creation of which is thought to assist the optically induced \( d-d \) transition in GdFeO\(_3\)-distorted manganites [32]. The evidence of the static polarons has been seen in the optical spectra for the polarons arising from the chemical doping [35] and under illumination with CW light at 2.3 eV [36].

The classical JT polaron is a local distortion in an otherwise non-JT-distorted lattice, which happens when an excess electron occupies one of the empty degenerate \( e_g \) levels. The lattice reacts locally by undergoing a local JT distortion, which in effect lowers the energy cost associated with the presence of the excess electron.

In manganites, where the lattice is strongly JT-distorted in a collective fashion, the presence of an excess hole or electron may lead to an opposite effect. Namely, in order to minimize the JT energy cost associated with different local electronic configuration of the central Mn ion due to the presence of an electronic defect, the lattice around rearranges so that the JT distortion is locally reduced or removed [39]. The system tries to regain some energy, which can happen in general by either delocalization of the defect or reducing the strain cost on the surrounding bonds. In manganites the latter effect leads to more favorable energetically situation. As an effect, the defect becomes strongly pinned, as the hopping would require moving along also the lattice distortion (which translates into strong electron-phonon coupling). This phenomenon has been shown to happen without the necessary presence of magnetic ordering [39]. Additional effects that are not included in this picture are: hole/electron delocalizing onto neighboring manganese ions, presence of orbital defects and spin canting. The latter effect may be significant in the magnetically ordered phases. It comes from the fact that the electron can further reduce the energy when the anti-parallel spins on the neighboring sites become canted away from their ideal positions, and therefore some delocalization energy may be gained due to easier hopping within the double-exchange mechanism. Such bound electron is thought to be accompanied with the local distortion of the spin system [40] and upon increasing the defect concentration the distortions may start to become coupled to each other (Fig. 1.14).

The presence of AJT polarons has been first used to explain the FM-AFM phase transition in the phase diagram of \((La,Sr/Ca)MnO_3\) with excess electrons coming from
1.7 Anti-Jahn–Teller polaron

Figure 1.13: (a) mechanism of creation of an AJT polaron via an intersite $d-d$ transition; (b) schematic illustrating the FC mechanism of the resonant Raman excitation in LaMnO$_3$ and experimental spectra (c) showing enhancement of particular phonon intensities [37, 38]

Figure 1.14: Local spin distortion around a localized Ca$^{2+}$ defect (open circle) in a LaMnO$_3$ magnetically ordered lattice.
Properties of perovskite manganites

chemical doping [39]. Later it was proposed to arise also upon the optical transition. Additionally, it has been shown that the process of creation of the AJT polaron, which is strongly localized and pinned, is associated with generation of multiple phonons. This effect happens via the process of resonant Raman scattering and leads to strong amplification of the amplitudes of the phonons sensitive to the JT distortion at the photon energies resonant with the corresponding electronic transition [37, 38].

It has been proposed that in such a resonant scattering process, first the Mn ion is promoted to an orbiton intermediate state; within the Franck–Condon principle, the nuclear positions should adapt to a new electronic configuration by emitting a phonon. For the AJT polaron, the lattice acquires large oxygen distortions from the ground state because of the strong self-trapping, and so vibrations related to the JT undistortion become activated (Fig. 1.13). Quantum-mechanically, the strongest resonance happens for the most probable intermediate state which occurs at $2\Delta$, and this corresponds to a transition to a vibrationally excited orbiton state (orbiton ground state is $\Delta$ in energy above the lattice ground state). This state in turn relaxes to the orbital ground state, but not necessarily its vibrational ground state. This results in $n$-phonon resonant Raman scattering activated by a single electron-phonon process. Contrastingly, ordinary Raman scattering allows $n$-phonon excitation only as a sequence of $(n-1)$ relaxation processes, with its amplitude smaller by $(n-2)$ orders of magnitude than for the resonant case.

Recent experiments on mixed-valence (Pr,Ca)MnO$_3$ suggest that apart from the AJT polaron, there is evidence of a Zener polaron [35]. The signatures of both species seem to be present in the NIR region of the optical conductivity spectra. The Zener polaron picture differs from the Jahn–Teller picture in the following: in the AJT scenario, the electron undergoes an adiabatic on-site JT transition and then adiabatic hopping onto the neighboring site. In the Zener scenario, the JT transition has a strong $p-d$ admixture, namely the ground state is a charge defect localized on the oxygen ligand between the two Mn ions, creating a species with equal Mn$^{3+x}$ configuration. It undergoes a JT transition onto the Mn site, and then hopping onto a neighboring oxygen. Additionally, a Zener polaron possesses a Mn–O–Mn bond with a smaller buckling angle than the undistorted structure.
1.7 Anti-Jahn–Teller polaron
Chapter 2

Multiferroics

2.1 Introduction

Multiferroics—materials, where two or more ferroic orders coexist—are very interesting materials to study. The research on them is not only motivated by the fundamental questions regarding coupling mechanisms between the ferroic orders, but also because of potential applications. In particular, multiferroic data storage devices may turn out to overcome the existing limitations of ferroelectric and magnetic data storage devices [41]. While for industrial applications it may be better to turn to heterogenic multiferroic materials, such as ferroelectric and ferromagnetic thin film heterostructures [42], where two orders couple together via strain, for fundamental science it is very important to study single-crystalline phases.

This chapter discusses main aspects of physics of multiferroics with special focus on the context of experimental work reported in Chapters 5–7. It discusses microscopic sources of multiferroicity, associated symmetry requirements and properties of IR-active spin excitations connected to the presence of the magnetoelectric coupling.

2.2 Microscopic sources of multiferroicity

In general, the coexistence of two or more ferroic orders in a multiferroic does not imply that they are strongly – or at all – coupled together (and the reverse, not all magnetoelectric compounds are multiferroic, such as magnetoelectric Cr$_2$O$_3$). The ferroic order may concern various degrees of freedom, but most interesting for applications are the multiferroics exhibiting simultaneously magnetic and electric ordering. It is, however, difficult to achieve the coexistence of these two orders, and even more difficult to achieve the coupling between them. This is because ordinary microscopic sources of magnetism and ferroelectricity exclude each other [43, 44].
2.3 Multiferroicity in spiral magnets

On one hand, in classical ferroelectrics (FE) the polarization may arise due to two main mechanisms: it is either a macroscopic ordering process of already existing dipole moments disordered in a high-temperature phase, or a collective lattice distortion due to “freezing in” of a particular phonon mode. The latter is an exhibition of a second-order Jahn–Teller effect, and whether a material will undergo such a deformation is decided by an interplay between short-range repulsive forces. The electronic system energetically would prefer to prevent the displacement of the ions, and the electronic system has a tendency to react to such displacement by forming covalent bonds and so stabilizing a displacement. This in turn puts constraints on the parity of the ground and excited states of the system and their energies. What is more, a ferroelectric material should be insulating, which puts bounds on the band structure.

On the other hand, the macroscopic magnetism is achieved by making use of valence spins of the $d$ or $f$ shell. First, magnetic systems are often metallic. Second, the band structure of magnetic insulators containing transition metal elements is such that the $d$ shells are partially filled, and this prevents the ferroelectric distortion from happening: both the top of the valence band and the bottom of conduction band have the same symmetry, as they are composed primarily of transition metal $d$-states. Additionally, the $d$-electrons in the valence shell are very repulsive. Overall, the repulsive Coulomb interaction overtake any gain in potential energy arising from ferroelectric distortion. Therefore the multiferroicity cannot happen in such materials.

This means that multiferroicity has to be achieved in a different way. Among different ways around this limitation are [41, 43, 45] to use $d$-shell ions to undergo a FE distortion, but $f$-shell ions for the magnetism, such as in (Eu,Ba)TiO$_3$ perovskites; use unconventional sources of ferroelectric polarization, such as electron lone-pairs (BiFeO$_3$), geometrically driven polarization due to off centering that does not rely on a formation of a covalent bond ($h$-YMnO$_3$, BaNiF$_4$), charge-ordering (LuFe$_2$O$_4$), non-collinear magnetic order (CrBeO$_4$, TbMnO$_3$).

The further discussion will be constrained to mechanisms characteristic for the spiral magnets, an representative of which is TbMnO$_3$.

2.3 Multiferroicity in spiral magnets

In spiral-magnet multiferroics the primary mechanism driving the rise of ferroelectricity is the magnetic order. As explained in previous sections, the cycloidal spin order is stabilized by a magnetic frustration, namely competition between the nearest-neighbor and next-nearest-neighbor exchange constants. Here the ferroelectric polarization is a secondary order parameter, obedient to magnetization, and these multiferroics are called “improper” or “type II”.
In this section we discuss microscopic sources for the ferroelectric polarization in a spin cycloid, symmetry considerations and the static magnetoelectric coupling. We take TbMnO$_3$ as a model example.

### 2.3.1 Ferroelectric polarization across the Mn–O–Mn bond

The rise of ferroelectric polarization in a spin cycloid is explained in the following way. Taking into account two spins canted in respect to each other on the symmetric Mn–O–Mn bond, one can calculate the spin supercurrent between them [46]. First, the crystal field anisotropy influences the symmetry of the spin states via spin-orbit interaction. Then one can consider the electron hopping process between the two Mn atoms via the oxygen ligand. Both processes involving one hole (double exchange) and two holes (superexchange) give rise to electric polarization across the bond, whose direction is given in general by $\vec{e}_{12} \times (\hat{e}_1 \times \hat{e}_2)$, where $\hat{e}_i$ is the direction of $i$-th spin and $\vec{e}_{12}$ is the displacement vector joining the two spins [46]. Sometimes the term $(\hat{e}_1 \times \hat{e}_2)$ is named “magnetic chirality vector”.

While this is a purely electronic effect, in addition, there is accompanying structural distortion across the bond, when the Mn–O–Mn bond already possesses some distortion from 180°. The source of it is the inverse DM interaction arising from the tilted spins. This further displaces the oxygens from their equilibrium position set by the structural constraints and stabilizes the electric dipole moment [47]. However the displacement is thought to be very small, on the order of less than 10$^{-3}$ Å [48, 49].

In general, this mechanism can lead to both net antiferroelectric and ferroelectric structures (See Fig. 2.1). In a spin cycloid though all the moments are aligned parallel, since the spins are rotating consecutively from one site to the other. Additionally, if all the cycloids run in parallel in the crystal, a net ferroelectric moment arises.

Figure 2.1: (a) KBN mechanism of spin-current producing ferroelectric moment even along a straight Mn–O–Mn bond [46]. Left: Net ferroelectric polarization including the IDM interaction in a spin cycloid (b) and AFE order in a canted AFM material (c)
2.3 Multiferroicity in spiral magnets

2.3.2 Symmetry considerations

The presence of multiferroicity demands special constraints to the symmetry of the system. In general, in order to achieve simultaneous magnetic and electric ordering, the time-reversal and spatial inversion symmetry must be broken, respectively. In detail, it can be looked at in different complementary ways.

First, one can treat the incommensurate system as quasi-continuous and spatially inhomogeneous. This is a good approximation for systems with long enough ordering wavevector. Mathematically it is expressed by terms in free energy (Lifshitz invariants) which transform like \( M_i \partial_j M_k \) and are coupled to polarization. In general these terms are often (but not always) associated with the rise of an incommensurate magnetic structure with a particular \( q \). It can be shown \([50]\) that a spin cycloid structure propagating along \( \hat{e}_3 \) with a wavevector \( Q \) and described as \((M_1 \cos(Qx), M_2 \sin(Qx), M_3)\) gives rise to an electric polarization pointing along \((\hat{e}_3 \times Q)\). The same mechanism is a source of polarization across a Néel domain wall. However it must be pointed out, that spatial inhomogeneity is not a sufficient condition, as the spatial inversion symmetry must also be broken (for example, there is no ferroelectricity in the sinusoidal spin-density-wave state, which does not break the inversion symmetry).

Second, an equivalent result is obtained using group theory and representational theory. When a vector \( k \) describes magnetic ordering in a crystal, the set of symmetry elements which leave \( k \) invariant is contained in a little group \( G_k \). The transformations of magnetic moments under symmetry operations in \( G_k \) are described by a set of matrices, which can be further separated into orthogonal irreducible representations (irreps) \([51]\). Upon a phase transition, magnetic order will arise following the symmetry of one of the allowed irreps.

In the \( Pbnm \) space group, only four irreps are allowed for the Mn atoms, which are located at the \( 4b \) positions in the unit cell \([52, 53]\). Here we follow the indexing of the irreps after \([18]\). The phase transition sequence in multiferroic orthorhombic manganites is as follows \([54, 55]\). Multiferroic manganites isostructural with TbMnO\(_3\) belong to \( Pbnm1' \) space group in high temperature paramagnetic paraelectric phase. Upon lowering the temperature they are subject to a phase transition to AFM paraelectric phase with the \( mmm \) point group (\( Pbnm1'(0b0)s00s \) in the superspace notation), and the irrep \( \Gamma_3 \) is being activated \([18, 54, 55]\). Upon lowering the temperature, the crystal undergoes a second order phase transition to the AFM ferroelectric phase with the \( mn2 \) point group (\( Pbn21'/(0b0)s00s \) in the superspace notation), and the additional irrep \( \Gamma_2 \) is activated. The symmetry analysis of allowed terms in free energy results in the conclusion that only the \( c \)-component of polarization is allowed, while the magnetic order is contained within \((bc)\)-plane \([54]\). A remark needs to be made here: while the real magnetic space group belongs to the \( mm2 \) point group, the oxygen displacements related to the \( mmm \to mn2 \) symmetry lowering are small enough that in practice in most cases
the analysis can be held assuming a paramagnetic \( Pbnm \) crystal structure.

The symmetry analysis also points out to the source of experimentally observed proper ferroelectric behavior of the \( \text{TbMnO}_3 \) crystal, such as divergence of dielectric permittivity and a critical exponent of \( \frac{1}{2} \) of electric polarization, although \( \text{TbMnO}_3 \) is an improper ferroelectric in a sense that ferroelectric polarization is not a primary order parameter [54]. Normally the secondary order parameter would couple to a primary order parameter in a quadratic fashion, as \( P \propto S^2 \). Here however the polarization couples in a bilinear fashion to magnetic waves corresponding to both irreps separately, so \( P \propto S_2 S_3 \), where \( S_2 \) is a magnetic wave described by \( \Gamma_2 \) (\( \Gamma_3 \)). Since one of them (\( S_3 \)) is already present above the FE phase transition, the polarization couples only to \( S_2 \) and behaves as if it was the primary order parameter. This is the source of the observed pseudo-proper ferroelectric behavior of \( \text{TbMnO}_3 \).

### 2.3.3 Magnetoelectric coupling and switching by external fields

The fact that the ferroic orders are coupled is expressed via the magnetoelectric coupling. For the case of static magnetoelectric (ME) coupling, the magnitude of magnetoelectric susceptibility \( \chi^{em} \) is limited by the magnitudes of the dielectric and magnetic susceptibilities (\( \chi^e \), \( \chi^m \) respectively). In the most stringent form it has to smaller than the geometric mean of both: \( \chi_{ij}^{em} < \sqrt{\chi_{ii}^e \chi_{jj}^m} \) [56].

The presence of the ME coupling leads to two possible pathways towards the multiferroic domain manipulation. One employs the reaction of one ferroic order to the static external field related to the coexisting ferroic order. This effect can be used to achieve static switching of the multiferroic domains upon application of the external field, namely inducing a ferroelectric domain switching upon application of external magnetic field, and control over magnetic domain upon application of external electric field. Second pathway takes advantage of the fact that the presence of the ME coupling leads to the existence of magnetic excitations termed electromagnons. They possess an IR-active component, and their frequency is located in the THz range, which is related to the energy of the ME coupling. These excitations will be discussed in detail in the next section.

For multiferroic \( \text{RMnO}_3 \) the phase diagram as a function of magnetic field looks as depicted in Fig. 2.2a. As a general feature of all multiferroic \( \text{RMnO}_3 \), there are transitions to both ferroelectric and paraelectric phases, depending on the direction of applied field. The sinusoidal phase cannot be destabilized using a magnetic field up to 15 T. \( \textbf{H} \parallel a \) induces a phase transition to ferroelectric phase with electric polarization along \( a \) axis. It has been associated with the flop of the whole spin cycloid (spin-flop transition). When magnetic field is applied along \( b \) axis, a transition into the ferroelectric phase with \( P \parallel a \) happens, however here the magnetic structure is under debate, as there is evidence that it may be conical [57] and not simply the \((ab)\)-cycloid [58].
2.3 Multiferroicity in spiral magnets

fields $\parallel c$, a transition to a canted AFM paraelectric phase happens. Comparing behavior of the different compounds [59] it can be concluded that the $H \parallel c$ transition destabilizes a crystal structure towards bigger ionic radii and towards the A-type AFM phase. Contrary, the smaller field $\parallel b$ is needed to destabilize the structure in DyMnO$_3$ than in TbMnO$_3$, the former being more close to the E-type part of the phase diagram.

The coupling of the magnetic field to the structure has been explained by taking into account the transition to the conical structure [50, 57] or assuming spin-phonon coupling via Zeeman effect [21, 57]. It has been demonstrated that magnetoelectric domains are preserved upon switching using magnetic fields [61]. Curiously, the direction of the field unambiguously determines the sign of the ferroelectric domain. This has been previously explained by experimental misalignments within the setup [19], but it is also grounded in the microscopic properties of the system [57].

The timescales of the ME switching process have not been investigated very thoroughly until now, although there are numerous examples of the switching with continuously os-

Figure 2.2: Phase diagram of TbMnO$_3$ in external magnetic field [59]. (b) Polarization switching in TbMnO$_3$ upon rotating the external magnetic field along the crystal c-axis [60]
cillating magnetic fields on a timescale of miliseconds to seconds in TbMnO$_3$ [60] (Fig. 2.2b), hexaferrite [62], Tb$_2$MnO$_5$ [63]. It has also been demonstrated that the magnetoelectric switching induced by electric field happens on a timescale of miliseconds in another spin-cycloid material MnWO$_4$ [64].

2.4 Spin waves and electromagnons

In multiferroics the presence of static ME coupling may be accompanied by a dynamic ME coupling. It gives rise to novel excitations termed electromagnons. They are magnetic excitations exhibiting an oscillatory electric-dipole moment, activated by electric—and not magnetic—component of light. Their presence has been predicted theoretically in the 70s [65, 66] and confirmed experimentally in 2000s [67]. Since then, electromagnons have been found in many multiferroic crystals such as other $RMnO_3$ [68], CuO [69], R$Mn_2O_5$ [70], hexaferrites [71], and have been associated with many interesting phenomena such as non-reciprocal directional dichroism or birefringence [72–74]. It has been even proposed that the multiferroic materials could be used as terahertz waveplates due to the rotation of the polarization of the incoming wave due to electromagnon absorption [75].

In general, the electric-dipole activity of electromagnons is confirmed by analyzing selection rules in optical methods, and their magnetic counterpart can be identified using neutron scattering (Fig. 2.3).

The following section describes the linear spin wave theory in spin cycloid compounds, as well as microscopic origins of electromagnons.

2.4.1 Spin waves in cycloidal magnets

In every magnetically ordered crystal there exist elementary magnetic excitations, analogous to lattice excitations in ordered crystals. It is a direct consequence of the symmetry breaking (Goldstone theorem [78]). The eigenmodes and dispersion relations are strongly dependent on the details of the magnetic ordering. Magnons can be experimentally observed, among other methods, using inelastic neutron scattering which gives access to the whole dispersion curve, and optical IR and Raman spectroscopy (due to the sensitivity of antiferromagnetic and ferromagnetic resonances to the oscillatory magnetic component of light, and the bimagnon excitation using a single photon).

While the analysis of the magnetic excitations for simple ferromagnets and antiferromagnets is relatively simple within the linear spin wave theory [78], such analysis for non-collinear incommensurate structures can be troublesome given the complexity of the Hamiltonian and non-trivial behavior of the Brillouin Zone.

For the spin cycloid, three main magnetic modes have been proposed theoretically [79] and their existence has been confirmed using unpolarized and polarized neutron
2.4 Spin waves and electromagnons

Figure 2.3: Temperature dependence of the energy of the electromagnons, comparing the IR (red lines) and neutron data (round symbols) [58]

Figure 2.4: Magnetic dispersion curves of TbMnO$_3$ measured with inelastic neutron scattering along different directions (a–c) and the spin-motion patterns associated with the 3 magnon branches (d) [76]. (e) Full magnon dispersion along the cycloid propagation vector [77]
scattering data [76, 77]. A detailed analysis within the formalism of the linear spin-wave theory for a magnetic Hamiltonian including NN, NNN interaction and single-ion anisotropy, using the co-rotating frame approach has been given in [80]. The dispersion curves and mode patterns can be calculated taking into account a relatively simple magnetic Hamiltonian, and approaching the incommensurability of the cycloid using the co-rotating-frame coordinate system.

Three modes are found to exist in the system:

1. linearly polarized excitation with wavevector $q$, equivalent to rotation of the spins about the $a$-axis. This excitation is a phason of the cycloid, with zero frequency, degenerate in energy, since for the incommensurate system in the static state, spins with all possible rotations within the cycloid exist.

2. two magnons with $q + Q$ and $q - Q$ ($\pm Q$ in the co-rotating frame), circularly polarized, where $Q$ is the propagation vector of the cycloid. These are degenerate in energy, and their anti-symmetric and symmetric combinations, which are linearly polarized modes, correspond to rotation of the spins in the co-rotating frame about the $c$ and $b$ axis respectively. All these modes carry non-zero dynamic magnetization and can be visible in optical spectroscopy as antiferromagnetic resonances.

Other approaches to the calculation of magnetic modes involve $\sigma$-model-like field theory [81] and Monte-Carlo simulations [82].

Experimentally measured dispersion curves for the three modes are summarized on Fig. 2.4, along with the schematic of the basic spin motions. Due to the fact that in reality the cycloid in $\text{RMnO}_3$ is not circular, these modes may mix with each other.

2.4.2 Microscopic origin of electromagnons

In spin cycloidal multiferroics, two main mechanisms of how the magnetic excitation in $\text{RMnO}_3$ can exhibit electric activity in an optical experiment are currently known. One explanation follows the spin current Katsura–Balatsky–Nagaosa (KBN) scenario [79] related to the net DM electric polarization of the spiral. Another mechanism includes symmetric exchange striction between pairs of the spins, creating finite oscillatory ferroelectric polarization [83].

There is no consensus on the phonon modes involved in producing the IR sensitivity of the electromagnons. There is mixed experimental evidence pointing to particular or all the phonon modes as giving their IR activity to the electromagnon [27, 84, 85].

DM mechanism

Due to the spin-current mechanism, canted spins produce electric polarization within the plane of the cycloid. If the whole cycloid undergoes oscillatory motion out of plane, the accompanying ferroelectric polarization should also oscillate, giving rise to electric activity of this magnetic excitation. It can be identified as the symmetric combination
2.4 Spin waves and electromagnons

Figure 2.5: Schematic illustrating the KBN scenario for the electromagnon. (a) blue plane represents the \((bc)\)-plane of the cycloid. (b) a cycloid plane in the ground state (left) and excited state of the KBN electromagnon showing polarization rotation coupled to oscillation of the cycloid plane.

of the \(\pm Q\) modes, described above. Because this excitation is geometrically tied to the plane of the cycloid, the selection rules depend on the orientation of the cycloid within the crystal. It has been shown that upon flop of the spin-cycloid plane from the \((bc)\) to \((ab)\) configuration, the selection rules of this electromagnon follow the orientation of the cycloid [83].

In MF manganites, the DM-originating excitations have been found in the 5–20 cm\(^{-1}\) range (0.15–0.6 THz, corresponding to wavelengths of 0.5–2 mm) [68, 84]. Out of the two optical absorption peaks visible in this range, the lower one has been identified to almost perfectly correspond to the KBN magnon visible in the neutron diffraction (Fig. 2.3). It is located at the magnetic A-type zone center (0 \(q\) 1). Optically this mode can be excited due to an umklapp process, where a photon with a zero wavevector can scatter off the static spin modulation with a particular finite wavevector, and therefore produce a magnon of the same wavevector; its source is third-order magnetoelectric coupling [86].

The intermediate peak visible in the IR has been assigned to another magnetic branch, however there exist some discrepancy between the optical and neutron data (Fig. 2.3) [58]. A difficulty behind reliable mode assignment is a relatively flat magnon dispersion in this region of reciprocal space. This optical absorption peak has been also speculated to originate from the high-harmonics and ellipticity of the cycloid [82].

Exchange striction

Another mechanism giving rise to the electrical activity of the magnon is associated with the mechanism of symmetric exchange striction. This interaction is the main source of static ferroelectricity in E-type multiferroic manganites; however, in spin-cyclodidal manganites its net static contribution to the ferroelectric polarization is zero due to the anti-ferroelectric arrangement of local polarization vectors on the neighboring Mn–O–Mn bonds. The following reasoning can explain why it can be a source of oscillatory polarization in manganites [83].
In the distorted perovskite lattice the oxygens in the Mn–O–Mn bonds are ordered in a characteristic, staggered fashion (Fig. 2.6). Oscillatory electric field polarized along one crystallographic direction moves the oxygen ions away from the relaxed bond geometry, decreasing or increasing the distortion of the bond. Since the net interaction between the manganese spins is mediated via the angle of the Mn–O–Mn bond, the oscillatory electric field also changes the effective exchange interaction between every pair of spins. This in turn results in the tendency of the spins to rotate to change their orientation compared to the static case. Therefore it can be understood that the pulse of electric field can give rise to subsequent oscillation of the spins.

Formally this coupling can be written in the following form:

$$H_{ME} = -gE \sum_{<i,j>} (\pm 1)S_i \cdot S_j$$  \hspace{1cm} (2.1)$$

where $g$ is a coupling constant, $E$ is the electric field and the sign of a particular $S_i \cdot S_j$ term depends on the geometrical details of the particular bond distortion [83]. Out of equation 2.1 it follows that $\pm gE = \Delta J$ is the modulation of the effective exchange constant, in the first approximation linear in $E (\cos(x) = x)$. The numerical value of $g$ can be estimated from the details of magnetic structure [87], and a field of 1 MV/cm corresponds to the changes of exchange constant on the order of 0.022 meV, which is approximately 3% of its static value.

Due to characteristic ordering of the $Pbnm$ lattice, if the oscillating electric field of light is applied along $b$- or $c$-axes, all the contributions are cancelled out and so overall there can be no magnetic excitation. However the field along the $a$-axis can give rise to spin oscillations, regardless of the orientation of the spin cycloid in respect to the crystal axes.
2.4 Spin waves and electromagnons

The initial motion of the spins can be deduced from looking at the pairs of Mn spins separately. When the bond is deformed towards $90^\circ$ angle, the spins tend to align more parallel, and so for the case of $(bc)$-cycloid the component of the spin along the bond line within the $(ab)$-plane will tend to be decreased, and the spin will move towards the $c$-axis (Fig. 2.6). Overall, all the rotations trying to precess the spins about the $c$ axis will cancel out due to staggering of the bonds. The effective net motion of the spins is the out-of-phase oscillation of the neighboring spins within the plane of the cycloid.

The IR absorption due to the Heisenberg exchange striction has been observed in the $40$–$80 \text{ cm}^{-1}$ range (1.2–2.4 THz, 125–250 $\mu$m) \cite{17, 83, 85, 88}. Contrary to the DM-mode, it has been associated with a zone-boundary excitation of the highest branch \cite{76}. There is some evidence from recent neutron measurements however that this excitation may in fact correspond to a $1-q$ excitation \cite{89}.
Chapter 3

TbMnO$_3$ as a multiferroic manganite

3.1 Introduction

Having discussed the basic physics of manganites and multiferroics, one can look at TbMnO$_3$ as a representative of both groups. This chapter describes the details of properties of TbMnO$_3$ in terms of magnetic structure, THz and optical spectra.

3.2 Phase transitions of TbMnO$_3$

As introduced in Chapters 1–2, TbMnO$_3$ lies in the phase diagram of manganites in a region where the competition between the nearest neighbor and next-nearest-neighbor AFM exchanges compete with each other. If only two magnetic exchange interactions were present, such a situation would result in only one phase transition, from the paramagnetic to the magnetically ordered cycloidal state. In TbMnO$_3$ however, the situation is more complex due to many additional weak interactions between spins. Such interactions are the biquadratic interaction (next-order term in the perturbation of the Heisenberg exchange Hamiltonian), single-ion anisotropy (setting easy and hard axes within the direct surrounding of the magnetic ion), higher-order Dzyaloshinskii–Moriya interaction and symmetric exchange striction.

Experimentally, it has been determined that at room temperature the TbMnO$_3$ crystal is in the orbitally-ordered, paramagnetic phase [15]. Upon lowering the temperature, there are two magnetic phase transitions, at 42 K (SDW, paraelectric) and 27 K (spin-cycloid, ferroelectric), connected to the Mn spin ordering. An additional transition related to the 4$f$ spins of the Tb ions occurs at 7 K [18, 90], and above that ordering temperature, the Tb spins follow the ordering of the Mn spins to the extent that they show Mn-spin domain sensitivity [91].
3.2 Phase transitions of TbMnO$_3$

Figure 3.1: Schematics of magnetic ordering in TbMnO$_3$ for (a) $42 \text{K} < T < 27 \text{K}$ and (b) $T < 27 \text{K}$. The size of Mn atoms has been reduced for clarity and ellipticity in (b) has been neglected. (c) Appearance of spontaneous ferroelectric polarization along $c$-axis upon crossing the $T_C$ [90].

Due to the strong magnetic interactions in the system, the short-range spin correlations persist in the paramagnetic state up to temperatures of 80–100 K. This effect can be seen in thermal conductivity and thermal expansion coefficients [92], spectral weight of the low-frequency spectral features below 4.2 THz [88], dielectric measurements [93], optical constants in the visible range [94] and pump–probe measurements probing the optical reflectivity [95]. All these results are coherent with the idea that the dynamic magnetic and lattice fluctuations are significant far above $T_N$. They are related to the spin-phonon coupling and may be also related to the formation of AJT polarons.

3.2.1 Details of magnetic ordering

As throughout the phase diagram of all manganites, in all the magnetically ordered phases the Mn spins are ordered AFM along the $c$-axis and FM along the $a$-axis. Overall, the wavevector of the magnetic structure of TbMnO$_3$ and its neighbors on the phase diagram can be described as $Q = (0 \ q \ 1)$, where $q$ ranges between 0.25–0.5.
At $T_N = 42$ K first phase transition occurs [96] with the spins forming a spin-density-wave state with incommensurate propagation vector of $q = 0.295$ along the $b$-axis (Fig. 3.1a). No apparent higher harmonic magnetic satellite peaks are observed in neutron diffraction [18], suggesting that this phase does not contain significant distortions from the sinusoidal spin length modulation. The propagation vector of the cycloid has a monotonic but not linear temperature dependence, first decreasing in $q$ with lowering temperature, and when approaching the next phase transition, around 35 K, the $T$-dependence is greatly reduced. The spin components in this phase are directed mainly along the $b$-axis.

The second magnetic transition happens at $T_C = 27$ K, which is a second-order transition to a spin-cycloid ordering with a finite ferroelectric polarization due to the KBN-IDM mechanism (Fig. 3.1b). The magnitude of the polarization is on the order of approx. 500–800 $\mu$C/m$^2$ and points along the $c$-axis (Fig. 3.1c) [90, 97]. The polarization direction is strictly tied to the helicity of the cycloid, which has been confirmed using electric-poling experiments using neutron or magnetic x-ray diffraction probes [97].

Compared to the SDW phase, the propagation vector of the magnetic structure becomes almost locked-in at $q \approx 0.28$, with very low-slope rise upon decreasing temperature. In this phase the spin order can be described as an elliptically deformed cycloid propagating along the $b$-axis. At 15 K, the spin components corresponding to irreducible representations $\Gamma_3$, $\Gamma_2$ (Section 2.3.2) are $m(\text{Mn})_{\Gamma_3} = (0, 3.9, 0) \mu_B$, $m(\text{Mn})_{\Gamma_2} = (0, 0, 2.8) \mu_B$ respectively [18]. For the Mn atoms located at 4$b$ positions in the unit cell, the $x, y, z$ components of the magnetic moment relate to the particular type of magnetic ordering [52]. Here $\Gamma_2 = (C_x, F_y, A_z)$, $\Gamma_3 = (G_x, A_y, F_z)$. Comparison with $m(\text{Mn})_{\Gamma_2}$, $m(\text{Mn})_{\Gamma_3}$ leads to a conclusion that the majority of the magnetic order is covered within the A-type magnetic ordering [98]. This is consistent with the fact that most of the sensitivity to the phase transition is seen in A-type reflections, following the extinction rule $h + k = \text{even}$, $l = \text{odd}$, for as (001) or (041), and their magnetic satellites. However, one can observe also weak reflections of the F, C, and G types, lower in intensity by 1–2 orders of magnitude [99], suggesting that there exist deformations to the dominant A-type structure.

From the ratio of $m_c/m_b$, the ellipticity in TbMnO$_3$ is estimated to be on the order of 0.7. This ratio becomes smaller when moving on the phase diagram further towards higher GdFeO$_3$ distortions, and correspondingly the $q$-vector becomes larger [100].

### 3.2.2 Additional spin order distortion due to the DM interaction

Interestingly, the dominantly A-type spin cycloid possesses a distinct deformation, encoded in the F-type satellites of peaks with extinction rules $h + k = \text{even}$, $l = \text{even}$ (in particular satellites of the (000) center) [101]. This contribution has been assigned to the additional deformations due to the DM interaction across the Mn–O–Mn bond,
3.2 Phase transitions of TbMnO$_3$

which acts on top of the perfect cycloid arising from the spin frustration. This interaction acts both in the SDW and MF phases and causes effective rotation of the spins within the $(bc)$-plane out of their equilibrium positions (Fig. 3.2). Because of the F-symmetry of these additional rotations, it destroys the AFM ordering along the $c$-axis; however, no weak ferromagnetism arises due to the incommensurability of the cycloid.

This effect has been found also on the theoretical grounds by analysing the magnetic exchange Hamiltonian of the system [20, 102]. It has been proposed that this additional modulation is a determining factor stabilizing the orientation of the cycloid in the $(bc)$-plane (containing a hard $c$-axis) instead of the $(ab)$-plane.

These results are also consistent with the increase of ellipticity of the cycloid with an increase in GdFeO$_3$ distortion, along with the appearance of a significant sinusoidal $c$-modulation in the SDW phase [100].

Interestingly, both A-type and F-type orders are very strongly coupled to each other: the ellipticity of the A-type and F-type cycloids are the same respecting the relation between the $b$ and $c$ components of the two cycloids (the A-type component along $c$-axis ($b$-axis) gains a $b$-axis ($c$-axis) contribution of the F-type). Additionally, the magnitudes of the magnetic components visible via resonant x-ray diffraction looking at the F-type $(0 \ q \ 0)$ and A-type $(0 \ q \ 1)$ satellites follow the same temperature and x-ray polarization dependence, including the electric-field poling sensitivity [101].

The magnitude of the F-type contribution (deviation from pure AFM 180$^\circ$ relation between neighboring spins along the $c$-axis by the angle $2\phi$) can be estimated by calculating $\tan \phi = |D_{DM}|/2J$ [101], where $D_{DM}$ is the DM constant and $J$ the AFM exchange constant, and assuming $D_{DM} \approx 0.3$, $J_c = 1.25$ [20], we obtain $\tan \phi \approx 0.12 \rightarrow \phi \approx 7^\circ$, consistent with the observation that intensity of the F-peaks is lower by 1 order of magnitude than intensity of the A-peaks.

3.2.3 Role of magnetocrystalline anisotropy

As mentioned above, low energy corrections to the simple Heisenberg Hamiltonian play a big role in stabilizing the effective magnetic order in the frustrated phases of manganites. It turns out that single-ion anisotropy plays a very strong role in influencing the equilibrium magnetic structure.

It has been calculated that the ellipticity of the spin cycloid is intrinsically connected with the magnetic correlations along particular crystal axes (Fig. 3.3). The $b$-axis correlations set in at the Néel temperature in the SDW phase and they continue to strengthen upon lowering the temperature, without being sensitive to the MF phase transition. At $T_C$, however, the $c$-axis magnetic moments acquire long-range correlation, and the spin-spin correlation function takes a finite value which increases towards lower temperatures. However, even at $T = 0$ K the ratio of the long-range spin correlation functions along $b$ and $c$ is predicted not to saturate at 1, but equilibrate at a finite value.
Figure 3.2: A-type (violet) and F-type (red) contributions to the spin ordering in TbMnO$_3$ for (a) SDW phase, (b) (bc)-cycloid phase [101]

with a ratio corresponding to the cycloid ellipticity measured using neutron scattering.

Phenomenologically, the $b$-axis acts as the magnetic easy axis of the crystal and it seems to have strong influence on the magnetic ordering process. It has been found to be much stronger than other anisotropic interactions [20]. Microscopically, it has been modeled in the scenario where alternating easy and hard magnetization axes of neighboring Mn ions within the (ab)-plane create a finite easy $b$-axis due to the GdFeO$_3$ distortion, and removing the distortion made the alternating terms cancel out completely [20]. Additionally, modeling the evolution of the magnetic structure without this interaction led to a direct phase transition from the paramagnetic to (ab)-cycloidal state. Alternatively, the same result was achieved by removing the GdFeO$_3$ distortion, and the SDW phase appeared upon inclusion of explicit easy axis along $b$. In this scenario it has been proposed that—as the temperature is lowered and the effective ordered moment increases—the $c$-axis moments emerge only when the NN-NNN frustration overcomes the energy gain due to satisfaction of the easy-axis anisotropy.

An alternative scenario has been developed by considering the fourth-order terms in the magnetic Hamiltonian, including various biquadratic interactions [103]. Here the best agreement with the DFT model has been found by introducing just one additional term containing strong negative (ab)-plane biquadratic coupling, which favors collinear alignment of the spins. In this scenario the microscopic mechanism does not involve magnetocrystalline anisotropy, but concerns the energy gain due to consecutive
hopping between NN ions within four sites.

Comparing the values for single-ion anisotropy calculated for a series of RMO, one notices that they are very well separated at the ends of the phase diagram corresponding to very big and very small ions (La, Lu). In the region of Gd–Ho they become very similar in magnitude [20]. This region correlates with the part of the phase diagram with strong mixing of the Raman $A_g(1/3)$ modes.

Strong single-ion anisotropy has been also proposed to be the source of a cycloidal distortion of the E-type magnetic structure, appearing in the phase diagram for smaller $R$ ions. The same mechanism has been proposed to add the symmetric-exchange-striction contribution to the (ab)-cycloid phase, and to add an antiferroelectric static component to the (bc)-cycloid phases [21]. Microscopically, these additional contributions come from additional displacements of the oxygens arising from the Peierls-type coupling within the Mn–O–Mn bond, modifying the FM exchange $J_{ab}$ acting between the NN within the (ab)-plane.

The same mechanism in a dynamic case has been also shown to significantly influence the electromagnon spectra. The dynamic $J_{ab}$ modulation has been assigned to be the main driving force for the optical activity of the zone-boundary electromagnon [82, 83]. This is consistent with the proposed scenario that it is coupled to the oscillating electric polarization arising within the symmetric exchange striction scenario.

Additionally, the calculations show that the low-frequency feature does not arise from the Heisenberg term containing only exchange and hard-c-axis term, and including the Dzyaloshinskii–Moriya term gives only a minor contribution in the expected spectral range. Defining $b$ as the easy axis, however, immediately gives rise to a strong spectral feature, with the strength correlating positively with the increasing degree of ellipticity of the spin cycloid. The electromagnon peak arising at a given ellipticity is then further significantly enhanced by the presence of biquadratic term in the Hamiltonian [82].
TbMnO$_3$ as a multiferroic manganite

Figure 3.4: Electromagnons in TbMnO$_3$ as seen using IR spectroscopy (a) [85] and Raman scattering (b) [104] in all combinations of polarization of electric and magnetic components of light along the crystal axes.

### 3.3 Electromagnon

In TbMnO$_3$ the highest spectral weight feature at 1.8 THz corresponds to the Heisenberg zone-edge electromagnon [83]. A lower energy feature at 0.7 THz has been assigned both to the DM-activated electromagnon [83, 105] and to the elliptical distortion of the spin cycloid [82], and potentially consists of both features overlapping at the same energy. It has been proposed that it arises from scattering at $q = Q - 2q_b$ [83].

Both electromagnons are visible in the far-IR spectroscopy in transmission geometry. Optical selection rules confirm that the excitation is activated by the electric component of light along the $a$-axis (Fig. 3.4).

Both high and low-frequency electromagnons are also visible in Raman scattering in the backscattering geometry, activated by $E \parallel a$, $b$, and additional excitation overlapping with the low-frequency electromagnon shows up for $E \parallel c$ (Fig. 3.4). It has been noted that the electromagnon is best visible in the Raman process for an excitation wavelength of 568 nm (2.183 eV) [106]. The high-frequency Raman feature is shifted slightly towards
3.3 Electromagnon

Figure 3.5: Predicted flop of the cycloid plane orientation, induced by a THz pulse. (a) $E_0 = +14 \text{ MV/cm}$, (b) $E_0 = +13 \text{ MV/cm}$.

higher frequencies than compared to the IR spectra. In both cases the electromagnons show up as much broader and weaker features in the spectrum than the phonon lines. Their magnetic activity is confirmed by comparison of magnon energies as seen via inelastic neutron scattering (cf. Fig. 2.3), and by tracking their dehybridization upon magnetic-field induced phase transition into the E-phase [107].

It has been predicted that an intense THz pulse in a resonance with the high-frequency electromagnon can transiently disturb the $J_{ab}$ exchange constant so strongly that it can lead to a magnetic transition. Within several picoseconds after the excitation, the spin-cycloid plane finds a new equilibrium position, either in the $(ab)$-plane or in the $(bc)$-plane with the opposing cycloid chirality [87] (Fig. 3.5). The very intense THz pulse modulates strongly the exchange constant $J_{ab}$ by the order of 50%, which follows with the dynamic change of the potential energy landscape. The spins move coherently towards a new cycloid orientation, which is a local minimum of the potential energy in the static case and upon application a THz field is a new absolute minimum, and become trapped in this orientation once the THz pulse is gone.
3.4 Optical properties

3.4.1 Static spectra

According to the optical ellipsometry measurement, the main features in the VIS range, predicted for all manganites, can be seen also in TbMnO$_3$ [94]. These are: the $d-d$ peak around 2 eV with a fine structure, unassigned to particular transitions and a 5 eV peak due to the $p-d$ transitions, with the former showing much stronger anisotropy in regard to the crystal axes than the latter. The temperature evolution of the transfer of spectral weight within 0.5–4.5 eV points to the additional transfer of number of carriers from the higher to lower energies within 110–40 K; in the pure paramagnetic phase and magnetically long-range-ordered phases the spectral weight is constant with temperature. Both magnetic phase transitions are visible mostly in the off-diagonal components of the dielectric tensor, which are sensitive to the breaking of symmetry between the RCP and LCP light. These components have a peak at 3 eV, persisting even deep in the paramagnetic phase. Its spectral weight is sensitive to both phase transitions when measured within the $(ab)$-plane, with the external magnetic field along the $a$-axis [94].

3.4.2 Pump–probe measurements

There has been a number of ultrafast pump–probe measurements on multiferroics [109–111]. Such experiments using an optical pump on spin-cycloid manganites, in particular $(bc)$-cycloid TbMnO$_3$ [95, 112] and $(ab)$-cycloid Eu$_{0.75}$Y$_{0.25}$MnO$_3$ (EYMO) [108], helped to reveal additional features of the optical absorption mechanisms and spin-lattice couplings in these materials.

It has been shown that the excitation with 1.55 eV pump as well as 3.1 eV pump, proposed to couple dominantly to the $d-d$ and $p-d$ processes respectively, leads to a very similar qualitative behavior [108]. This similarity has lead to a conclusion that in fact both processes may create a population of Mn$^{2+}$, Mn$^{4+}$ ions, and the transfer of electron
3.4 Optical properties

Figure 3.7: (a) A pump–probe trace showing anisotropic transient change in reflectivity at 1.55 eV in TbMnO$_3$ upon excitation with 3.1 eV pump. (b)–(c) Relaxation rate as a function of temperature for TbMnO$_3$ [95] (b) and for EYMO [108] (c).

to create the Mn$^{2+}$ ion within the $p$–$d$ excitation process is followed by the process where a second electron jumps from the unexcited Mn$^{3+}$ ion onto the hole of the excited ligand.

The time-dependent change of reflectivity exhibits anisotropic behavior, and along the AFM $c$-axis the optical excitation leads to relative increase of reflectivity, and within the FM ($ab$)-plane to corresponding decrease [95, 108].

Interestingly, although covering the same spectral features in materials with very similar physics, there is no agreement whether the transient optical reflectivity is sensitive to magnetic phase transition temperatures (Fig. 3.7b). In TbMnO$_3$, the responses of the crystal both along $a$- and $c$-axes show the change of slope of the reflectivity transient at $T_N$ and $T_C$ and the relaxation rates have a clear anomaly at $T_N$. Contrary, in EYMO such behavior is not observed and the transient behavior is dominated by the short-range spin-spin correlations, setting in already far above $T_N$, and changing smoothly across the phase transition. One reason for this discrepancy may be different net sensitivity to the magnetic ordering when probed along particular crystallographic axes and

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when probed along the direction somewhere between them, or a particular combination of pump and probe wavelengths giving slightly different sensitivity to spin structure. In thin films of TMO exhibiting competing cycloid and FM phases, the anomaly of the relaxation time at the phase transition has been explained based on the fact that the magnetic subsystem will experience an anomaly in heat capacity and critical slowing down upon approaching the transition [112]. In both cases, the relaxation times strongly increase upon lowering temperature, asymptotically reaching 17 ps in TMO and 50 ps in EYMO.

The amplitude of the effect has been suggested to correlate with the nearest-neighbor spin-spin correlations, which increase when the temperature is lowered [108, 112].

The spin-lattice coupling has been confirmed to play a significant role in the optical excitation process in manganites. First of all, a direct evidence of the coupling between the d–d transition and the JT distortion has been seen in LaMnO$_3$ [8], where 2 eV pump is creating a population of coherent phonons related to the JT distortion and rotation of octahedra, strongly supporting the scenario of the AJT polaron formation (Fig. 3.8). In EYMO similar mechanism has been proposed as an origin of the long relaxation times, which relate the combined lifetime of the Mn$^{2+}$ and Mn$^{3+}$ polarons: spin-phonon coupling increases with lowering temperature, as seen via Raman measurements, and in the same time hinders the decay of the localized spin excitations, strongly trapped by the surrounding lattice. In frequency space, this corresponds to narrowing of the electron spin resonance lines in magnetically ordered manganites [108].
3.4 Optical properties
Chapter 4

Experimental methods

4.1 Introduction

Chapters 1–3 gave an introduction into the physics of TbMnO$_3$ necessary to understand the experimental results. Here we turn to the description of experimental methods, used to obtain results related in Chapters 5–7.

The main experimental method employed is a pump–probe technique, whose principle is described in Section 4.2. The subsequent section describes methods of generation of ultrashort pulses, with a special focus on the ones used in the experimental work, which produce pulses in three parts of the electromagnetic spectrum: visible, THz and soft x-ray range. In further sections we discuss specific methods applied in a time-resolved fashion in Chapters 5–7. We start from the overview of principle of resonant x-ray scattering in magnetic materials, which was used as a probe in Chapters 5 and 6. Then we turn attention to the methods used in Chapter 7 to detect changes in optical properties of solids with special focus on the time-resolved detection of Raman scattering probed at wavelengths on and off the electronic resonance. Next we describe mechanisms for generation of coherent excitations, such as phonons and electromagnons; such excitations were generated in Chapters 5 and 7. We finish the chapter with a brief description of the sample preparation, which was shared for all the performed pump–probe measurements.

4.2 Pump–probe technique

Time-resolved measurements are a complementary tool to the typical static measurements performed in adiabatic conditions. They rely on the mechanism of strongly disturbing the sample out of equilibrium and subsequent relaxation of the sample to the equilibrium state. In the most insightful configuration, the sample is disturbed in a selective way, so all the energy is most likely deposited only in one degree of free-
4.2 Pump–probe technique

Figure 4.1: Principle of a pump–probe experiment.

dom (spins, lattice, electrons...); then the energy transfer and change of the state of the sample is tracked by looking at physically measurable properties.

The easiest way to investigate the dynamics of a particular physical property of the sample is to record a movie - that is, disturb the system out of equilibrium and take the measurements of the property at particular points in time after the disturbance. This scheme however does not work for the processes which are comparable or faster with the response times of the detectors and other scientific equipment. In such cases, a pump–probe scheme must be used (Fig. 4.1). Most commonly it is used in a setting where the probed property of the sample can be accessed using electromagnetic radiation within high range of wavelengths (far-IR to hard x-ray), but can also employ short bursts of electrons to perform electron diffraction. The physical process happening after the excitation determines the choice of the probed property, such as optical transmittivity and reflectivity, birefringence, generation of higher harmonics, Faraday rotation, magneto-optical Kerr effect; when probing with x-ray diffraction, one has direct access to the correlation length, ordering wavevector and structure factors of charge, spin, orbital and lattice degrees of freedom.

In a pump–probe scheme one uses two pulses of electromagnetic radiation. First, a pump pulse disturbs the sample. The probe pulse is incident upon the sample with a particular delay $\Delta \tau$ in respect to the pump pulse. Experimentally this may be achieved by changing the optical length between the two beams by the means of electronic devices or mechanical delay stages. The probe beam, containing the information about the state of the sample, is then detected and one experimental point is recorded. Afterwards, the experimenter waits until the sample comes back to the equilibrium (typically the time on the order of a millisecond) and repeats the measurement, but now with a different delay between the two pulses. Afterwards, the whole dynamics can be recovered with the time resolution corresponding to the intrinsic time width of the pump and probe pulses and the time jitter between them.

One big advantage of the pump–probe method is a relatively easy and controlled way to investigate the properties of the samples in the non-linear regime. By increasing the pump fluence, one can strongly drive the system out of equilibrium to the area in potential energy landscape where simple parabolic approximation is no longer valid.
Experimental methods

Such experiments not only use optical pulses to excite electronic transitions, but also take advantage of using intense radiation in the mid-IR-THz regime in order to achieve coherent control of the desired properties of the sample. Such pulses used in a spectral range non-resonant with any absorption features may be used for example to manipulate the direction of magnetization [113]. Alternatively, when such an incident pulse is in a resonance with a lattice or spin excitation, it can be used as a supplementary spectroscopical tool [114, 115] or drive the phase transition in a subtle way involving significantly little heat [3, 116].

4.3 Generation of ultrashort electromagnetic pulses

Typical processes in solids may have time-scales differing by few orders of magnitude, with the purely electronic processes happening on the atto-femtosecond scale, the phonons and magnons ranging between few tens of femtoseconds and few picoseconds, and the propagation of heat and strain on the order of up to nano- and microseconds [117]. These timescales demand the use of ultrashort pulses of electromagnetic radiation. Luckily nowadays this can be achieved using table-top commercial ultrafast laser setups, to cover the range of far-IR to UV. The ultrashort x-ray pulses in the range from soft to hard x-rays are available in specialized setups at particular beamlines in synchrotrons and free electron lasers.

4.3.1 Optical range

There exists a variety of commercially available ultrafast lasers, producing pulses in the optical range with lengths on the order of 100 fs. The measurements done in this thesis were obtained using Ti:Sapphire lasers, producing ultrashort pulses with center frequency of 1.55 eV. Ti:Sapphire as a gain medium is very common due to good mechanical and optical properties of the host lattice and broad tuning range and high emission cross section of the Ti$^{3+}$ dopant.

To generate ultrashort pulses, these lasers operate on the Kerr-lens passive mode-locking principle [118]. The cavity of such a laser is designed in a way that it allows for only one transverse mode and a series of longitudinal modes. The longitudinal modes are forced to become locked at a given phase in respect to each other in order to achieve interference between the components of the electromagnetic field inside the cavity. This mechanism creates a train of ultrashort pulses, which are then coupled out of the cavity by a semi-transparent mirror. Technically mode-locking is achieved by a periodic modulation of the nonlinear medium inside the cavity, synchronized to the round-trip time. In case of passive Kerr-lens mode locking, this effect happens spontaneously as the intensity of the light propagating through the medium causes change of index of
refraction and respectively focussing of the beam, which causes only the mode-locked pulses to survive in the cavity.

The pulses coming out of the oscillator need to be further amplified, in order to reach desired intensity. This is done with regenerative amplifying schemes, where the pulses are trapped inside the resonator and make several passes across a pumped gain crystal (typically another Ti:Sapphire), gaining energy with each pass. In the end it is released from the resonator via an electro-optic switch. Additionally, more stages of amplification may be needed, and they may employ single-pass amplifying schemes as well. In order to protect the optical elements from damage by very high peak powers of the pulses undergoing amplification, the pulses are stretched before the amplification stage and re-compressed afterwards.

To achieve wavelength conversion, schemes basing on nonlinear optics need to be used. In particular, to cover the wavelength range in the IR regime (1–2\,\mu m), one needs to use an optical parametric amplifier [118]. In the process of parametric amplification, which is an inverse of a sum frequency generation, a pump photon is creating a signal and an idler photons with the frequencies following the energy conservation. With multi-stage amplification schemes, the resulting pulses can have energies only on the order of magnitude lower than the pump beam.

### 4.3.2 THz range

The THz frequency range is located between the microwave and infrared regimes, and in the past has been covered in some of the far-IR experiments. It is of high scientific importance, because it covers many low-lying magnon and phonon modes, including soft modes, and so not only interesting because of spectroscopy, but also because of a possibility of coherent control.

Among main difficulties in obtaining ultrashort and intense THz pulses are: poor phase matching in most of materials used for nonlinear optics, preventing efficient generation via nonlinear processes and consequently requiring very high powers of the initial optical beams; significant absorption by water molecules in air and low-lying phonon resonances of most crystalline transparent materials; cumbersome detection of beam position and its characterization. Due to recent technological advances, many of these obstacles could have been surpassed and many THz sources and materials are nowadays available commercially.

Among methods overcoming the phase matching problem, several solutions have been developed, such as optical rectification with pump pulse front tilting [119], or specially designed crystals. In the process of optical rectification, the incoming radiation produces a nonlinear polarization inside the crystal, which contains a DC component; in a case of an ultrashort pulse, the DC component corresponds to the envelope of the pulse, which falls in the THz regime.
In the experiments described in this thesis, the THz pulses were generated using optical rectification in organic crystals of 4-N,N-dimethylamino-4’-N’-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate (DSTMS) [120, 121]. These materials exhibit a very good phase matching and electro-optical coefficient, leading to efficient generation of the THz pulses when pumped with the 1.2–1.6 \( \mu \)m IR laser pulses [122, 123]. Additionally, the THz polarization can be set almost freely by rotating the optimally cut crystal about the incident beam pointing, parallel to the surface normal, and THz pulses with the opposite phase can be achieved by rotation of the DSTMS crystal by 180°.

One of the common ways to detect the THz pulses is to perform the electro-optical sampling, which is in itself a THz pump–optical birefringence probe experiment [124]. Here the electric field of the THz pulse is treated classically; when incident on the crystal exhibiting a finite electro-optic effect (such as ZnTe or GaP), the electric field creates a transient modulation of the refractive index of the crystal, following the THz waveform. This modulation can be read out by looking at the change of birefringence in the electro-optical crystal. Knowing the refractive indices of the crystal, its length and the relative modulation of the transmitted intensity, one can recover the absolute value of the electric field of the THz pulse. The absolute sign of the phase however is ambiguous, and without further modifications to the detection scheme, the electro-optic sampling can only give information about the relative change of phase, for example it can distinguish between two pulses shifted in phase by 180° in respect to each other, but it will not be able to assign an absolute sign to either of them.

4.3.3 X-ray range

Ultrafast x-ray pulses can be now achieved in several different methods. In an optical lab, they are realized using complex high-harmonic setups [125]. In synchrotrons, where the x-rays already have a long pulsed structure, there exists methods relying on introducing additional special bunch of electrons (camshaft) into the total filling pattern; this bunch is then further modified to achieve much shorter pulses, with the low-alpha setups realizing x-ray pulses several ps long, and slicing setups achieving time resolution down to 100 fs at the expense of x-ray pulse intensity. In the free electron lasers, the lasing process intrinsically produces ultrashort pulses and with long enough accelerators, one can reach the hard x-ray regime.

In this thesis, the x-ray measurements were performed at the Linac Coherent Light Source x-ray free electron laser, and at the Diamond Light Source synchrotron employing the low-alpha mode.

Synchrotron in a low-alpha mode

In the synchrotron-based methods, the length of the x-ray pulse is determined by the spatial length of the electron bunch. One obstacle in minimizing it in order to obtain ultra-
4.3 Generation of ultrashort electromagnetic pulses

short pulses is the Coulomb repulsion between the electrons in the bunch. However, one can tune the momentum compaction factor $\alpha$, which relates the momentum deviation, beam dispersion and the geometrical parameters of the optics. When $\alpha$ becomes low enough, the relativistic beam of electron finds a new equilibrium in a bunch which is longitudinally much shorter than an ordinary “high-alpha” rf bunch. However, this is achieved at the expense of the transverse length and leads to significantly higher deviation of transverse beam position, creating a need to implement additional feedback mechanisms [126]. This method produces x-ray pulses of moderately weak intensity, and at Diamond Light Source it gives the pulse length on the order of 10–20 ps FWHM.

X-FEL

The operating principle of an FEL relies on a positive feedback loop between the electron bunch in an undulator and the electromagnetic radiation emitted by it [127, 128]. In an undulator, travelling electron emits electromagnetic field due to the action of alternating magnets. When located within an electron bunch, the emitted waves will interfere leading to the fact that only particular radiation wavelengths will be sustained. In case of no interaction between the field and the electrons, all the electrons emit the radiation incoherently. In a real situation the electron bunch and emitted radiation form a self-consistent system, where the coupled forces of the undulator and electromagnetic radiation drive the motion of the electron, and the motion of the electron is a source of radiation. This phenomenon leads to slow exchange of energy between the electrons and the field over many undulator periods, eventually causing the electrons to form microbunches within the bunch, which have the periodicity of the radiation wavelength. This leads to coherent amplification of the emitted radiation.

In case of real systems, the electron pulse has a typical charge of 1nC and duration of 10–100 fs, which corresponds to tens of thousands of radiation wavelengths. The microbunching process will be initiated by noise separately in different regions of the main bunch. This eventually leads to creation of many coherent regions emitting phase-uncorrelated spikes of coherent radiation, typically over a hundred per pulse. This process, termed self-amplified spontaneous emission (SASE), creates pulses which have good transverse coherence, poor longitudinal coherence and stochastic multi-spike structure in both time and frequency. In case of SASE pulses, Fourier-transform limited pulses can be achieved with a monochromator placed further downstream, however accompanied with reduction of pulse intensity. In order to achieve the FT-limited pulses already at the stage of lasing, a seeding scheme may be introduced, where an external pulse is used to start the microbunching process in a controlled fashion. This can be done either by using a pulse from an ultrafast optical laser, or by introducing a monochromator for the x-ray beam and a chicane for the electron beam half-way in the undulator, in order to seed the downstream part of the undulator with the Gaussian pulse coming from
the first part.

One clear advantage of using an XFEL is high pulse brilliance (over ten orders of magnitude higher than the third-generation synchrotron sources) and intrinsically short pulse duration. Among the challenges, especially for the SASE pulses, are the high fluctuation of pulse intensity, and stochastic nature of the pulses, which average to a Gaussian pulse only statistically. Furthermore, the time jitter between the x-ray and optical pulses used in the experiment at the beamline can be very significant and order of magnitude larger than the pulse length, hence the need to monitor and control it using supplementary setup.

4.4 Resonant x-ray scattering

Results of this work reported in Chapters 5–6 have been obtained using time-resolved resonant x-ray scattering probe. Therefore a brief overview of this method following [129–131] is presented here.

Resonant x-ray scattering is one of the methods most suitable to investigate magnetism of the 3$d$ atoms. In general, it combines the principle of the ordinary x-ray diffraction by looking at the long-range order by use of Bragg scattering [132], with the element selectivity by using x-ray beam with the energy resonant with particular atomic absorption edge (Fig. 4.2).

In case of magnetic compounds, one can gain the most insight via resonant diffraction using the oxygen $K$-edge, transition metal $L$-edge and rare-earth $M$-edge.

The oxygen $K$-edge gives information about spatial modulations of the O 2$p$ states. Scattering experiments performed at this edge are typically not very sensitive to the ordering of magnetic moments, however the magnetic sensitivity becomes strongly enhanced in crystals which exhibit strong hybridization of oxygen ligands with orbitals of neighboring magnetic ions.

Transition metal $L$-edges correspond to the 2$p\rightarrow3d$ transitions to the valence states. Because of the spin-orbit interaction in the 2$p$ states, the probed 3$d$ states contain information about the spins. Additionally, the insight into orbital and charge degrees of freedom may be gained due to their influence on the configuration of the 3$d$ shell.

Figure 4.2: Principle of the RSXS process
Rare earth $M$-edges correspond to the $3d \rightarrow 4f$ transition, and due to the strong spin-orbit interaction on both shells, is very sensitive to $4f$ magnetism.

### 4.4.1 Scattering length in resonance

The diffraction off the long-range ordered lattice is described using a form factor (scattering length) $f_n$, in the most general case taking a form of

$$ f_n = f^T_n + f^M_n + \Delta f_n $$

where $f^T_n + f^M_n$ is a non-resonant contribution due to the Thomson and magnetic scattering, and $\Delta f_n = \Delta f'_n + i \Delta f''_n$ describes the contribution due to the atomic resonance ("dispersion correction"), which is dependent on the energy ($\hbar \omega$) and polarization of the incident and scattered beam ($e, e'$ respectively). The physical meaning of the scattering length corresponds to the change of amplitude and phase which the incident wave suffers from the process of scattering. In general, the scattering length can be related to the index of refraction $n = 1 - \delta + i \beta$ such that $1 - \delta \propto \text{Re}(f_n)$, $\beta \propto \text{Im}(f_n)$.

Throughout this analysis, the kinematic approach to the diffraction process is assumed. This is justified by the very weak intensity of the magnetic diffraction peaks and little contribution from the multiple photon events, and the refraction of the beam inside the sample is neglected.

The intensity of the scattered beam depends on the scattering vector $Q$ and is dependent on the two contributions: a unit cell structure factor, summing out the scattering from different entities within the unit cell, taking into account their form factors $f_n$ and positions $r_n$, and the lattice sum due to the interference from the unit cells within the probed volume (located at positions $R_m$):

$$ I(Q) \propto \left| \sum_n f_n(h\omega, e, e') \exp(iQ \cdot r_n) \right|^2 \times \left| \sum_m \exp(iQ \cdot R_m) \right|^2 $$

In the case of perfect translational symmetry, corresponding to the infinite coherence length, the second term becomes a sum of delta functions, and the deviation from the perfect coherence introduces a finite peak width.

The scattering geometry is set by the $k$ vectors of the incident and scattered beams, setting the scattering plane. The polarization within the scattering plane is customarily denoted as $\pi$, and perpendicular as $\sigma$. Analysis of the polarization dependence of scattering gives further insight into the intrinsic order in the sample.

The scattering length can be calculated theoretically via expression on the scattering differential cross-section, since $d\sigma/d\Omega = |f|^2$. Taking into account the coupling of the photon field with the electrons in the form of $p - eA/c$, one can estimate the probability of the photon to be scattered into the solid angle $d\Omega$:
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\[ \frac{d\sigma}{d\Omega} = r_0^2 \left| e \cdot e' < G|\rho(Q)|G > -m \sum_I \frac{< G|e' \cdot J(k')|I > < I|e \cdot J(-k)|G >}{E_I - E_G - \hbar \omega - i\Gamma_I/2} \right|^2 \]  \hspace{1cm} (4.3)

Here \( r_0 \) is the classical electron radius, \( \rho(Q) \) is the Fourier amplitude of the charge density at \( Q = k' - k \), \( |G>, |I > \) are the ground and intermediate states of the scatterer with corresponding energies \( E_G, E_I \), \( \Gamma \) is the lifetime of the intermediate state and \( J(k) \) is the current operator describing the virtual transitions between these states.

In this expression, first term corresponds to the non-resonant Thomson scattering from the charge density \( \rho \). The second term contains two successive transitions, where an incoming photon is annihilated and scattered photon is created. Because of the energy dependence in the denominator, with the photon energy resonant with the transition energy between the two states, this term may completely dominate the scattering cross-section.

4.4.2 Scattering off the magnetic atom

Taking into account dipole transitions, the resonant scattering length can be rewritten in the following way, to write out the polarization dependence in a more explicit fashion:

\[ \Delta f = F^{(0)} e^{\prime \ast} \cdot e - iF^{(1)} (e^{\prime \ast} \times e) \cdot \hat{s} + F^{(2)} (e^{\prime \ast} \cdot \hat{s})(e \cdot \hat{s}) \]  \hspace{1cm} (4.4)

Here \( F^{(0,1,2)} \) are the photon-energy dependent resonance factors, and \( \hat{s} \) is a unit vector defining the direction of the spin. The first term corresponds to a non-magnetic resonant scattering, adding up to the Thomson term and contributing to the Bragg peak. Two other terms describe a magnetic resonance process. The second term, linear in \( \hat{s} \), can be related to x-ray magnetic circular dichroism, and produces first-harmonic magnetic satellites. The third term, containing two powers of the magnetic moment, is related to magnetic linear dichroism and produces the second-order magnetic satellites. The magnetic satellites arising around the particular peaks give information about components of magnetic structure.

In crystals, the \( \Delta f \) will be a tensor \( \Delta \hat{f} \) with the allowed components dependent on the local point group symmetry of the scatterer, however as long as the term linear in \( \hat{s} \) dominates the signal, cyllindrical approximation is often sufficient.

In order to calculate the polarization dependence, the scattering length can be rewritten in a following fashion

\[ S = \begin{pmatrix} \epsilon_{\sigma}^{t} \cdot \Delta f_{\sigma}^{t} \cdot \epsilon_{\sigma}^{t} & \epsilon_{\sigma}^{t} \cdot \Delta f_{\pi}^{t} \cdot \epsilon_{\pi}^{t} \\ \epsilon_{\pi}^{t} \cdot \Delta f_{\sigma}^{t} \cdot \epsilon_{\sigma}^{t} & \epsilon_{\pi}^{t} \cdot \Delta f_{\pi}^{t} \cdot \epsilon_{\pi}^{t} \end{pmatrix} \]  \hspace{1cm} (4.5)

where \( S \) is a \( 2 \times 2 \) matrix separating the particular contributions arising with the incident light with polarization \( \epsilon \) and scattered light with polarization \( \epsilon' \).
### 4.4.3 Multipole expansion

In many cases, a simple approximation for spins using a stick model—where magnetic moments are represented by arrows or sticks—is enough. More exact calculation of the scattering lengths of the atoms, spins and orbitals may be performed using a multipole expansion. This approach takes into account that the shape of the electronic cloud is distorted by the local crystal field. This shape is modeled using decomposition into spherical harmonics and spherical Bessel functions. The rank $K$ of the spherical harmonic corresponds to a particular multipole, and $K = 1$ corresponds to a dipole, $K = 2$ a quadrupole etc. The quadrupole scattering probes the asymmetry in charge distribution, and can be related to the orbital scattering, as it probes final states, whose orbitals are affected by the orientation of ions in space [133].

For convenience, the multipoles can be rewritten using quantities $A_{K,Q}, B_{K,Q}$, corresponding to even and odd functions of the projection $Q$ respectively ($-K \leq Q \leq K$). In this way one takes into account a distribution of charge and magnetism. Symmetry arguments regarding spatial and time inversion symmetry help in interpretation of the resonant x-ray scattering signal. One big advantage of this method is that it can explain additional scattering for positions which are forbidden following the simple description.

More advanced techniques of resonant scattering include not only electric dipole events, but also electric and magnetic dipole events or higher order quadrupole events, and can reveal atomic polar and magneto-electric multipoles [134].

### 4.5 Optical methods

In Chapter 7 we use transient reflectivity as a probe for the spectral dynamics and a tool to observe coherent oscillations, which we attribute to coherent phonons generated by the pump pulse. This section discusses in general terms the optical properties of solids and description of the Raman process in resonance with an electronic transition.

#### 4.5.1 Optical reflectivity of solids

The optical reflectivity of a solid is an observable which is relatively simple to measure, in the same time giving plenty of information about the processes happening in a solid. It depends directly on the complex dielectric constant and the complex refractive index of a medium. On the side of a probing beam, these quantities tell how the propagation of electromagnetic wave is affected by the surrounding material. On the side of a solid, these parameters may be related to certain properties of the material and its microscopic properties.

In the absence of excitations, the electric field of light induces a polarization in a crystal, which in a linear case are related by the linear dielectric susceptibility tensor $\chi$, 

- **4.5 Optical methods**
\( \mathbf{P} = \varepsilon_0 \chi \mathbf{E}_f \). On the other hand, the electric field is related to the dielectric displacement \( \mathbf{D} = \varepsilon_0 \mathbf{E} \). The dielectric permittivity in a linear case is related to permittivity via \( \varepsilon = \varepsilon_0 (1 + \chi) \) and for dispersive media, they are both functions of \( \omega \). In the simplest case of isotropic system, the refractive index \( \tilde{n} = n_1 + in_2 \) is a square root of the complex dielectric constant \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) and reflectivity of the crystal at normal incidence is \( R = \left| \frac{1 - \tilde{n}}{1 + \tilde{n}} \right|^2 \). In case of anisotropic crystals, \( \varepsilon \) is a tensor and is connected with the refractive index \( n \) via Fresnel’s equation. In case of biaxial magnetic crystals, the general expressions for reflectivity become much more complicated [135].

The structure in optical spectra can be understood within the formalism of joint density of states. In case of interband transitions of the electrons in insulators, quantum-mechanically it can be understood that the absorption strength by a given transition will be related to the probability of such a transition, which in turn is related to the joint density of states. It is a quantity defining number of states per unit volume and unit energy range, which occur when the energy of the photon is equal to the energy difference between the conduction and valence bands. The joint density of states will diverge at different points of the Brillouin Zone, producing structure in the frequency dependent optical property of the solid. The most effective transitions happen near band extrema, where the bands are parallel over a region of \( \mathbf{k} \)-values.

**Ellipsometry**

In Chapter 7 a measurement of the dielectric constant of the sample was performed in an ellipsometric measurement in order to supplement the pump–probe data with the information about the optical properties of the crystal in thermodynamic equilibrium without the pump excitation. Here we briefly discuss the basic principles of the technique.

Ellipsometry [136] is one of the experimental methods used to obtain the values of dielectric constant. In general, because of the complex nature of the \( \varepsilon \), a measurement only of a single parameter like reflectivity or transmission is not enough to recover its both real and imaginary components. Different schemes are used in order to overcome this limitation, for example by measuring absorption or transmission in addition to the reflectivity, or collecting data at more than one incidence angle. When the spectra are collected over a large range of frequencies, the Kramers–Kronig transformation, relating \( \text{Re}(\varepsilon) \) and \( \text{Im}(\varepsilon) \), can be used. Additionally, one can perform numerical fitting of the data, for example using Eq. 4.6.

In an ellipsometric technique one is able to measure the complex dielectric constant of a solid in a single measurement. Linearly polarized light, with the polarization being neither within or perpendicular to the scattering plane (\( p, s \) respectively) hits the sample at a particular angle. The reflected light is polarized elliptically and a complex value of the ratio of \( p \) and \( s \) reflectivities is measured. From these quantities one can recover the dielectric constant of the sample at a particular energy, and the rotating analyzer...
4.5 Optical methods

scheme makes it possible to perform the measurement only at a single incidence angle. The measurement is performed in a range of photon energies, and in case of crystals, the orientation of the sample is controlled.

To analyse the structure of the dielectric constant obtained in an ellipsometric measurement, the Lorentz model is often used, which is the simplest way to model the optical response of a solid. Following the classical equation of motion for an electron bound harmonically to a mass and driven by an optical electric field, one arrives at the Lorentz relation giving the simplest theory of the optical constants:

$$\tilde{\epsilon}(\omega) = \epsilon_\infty + \sum_j \frac{A_j^2}{\omega_j^2 - \omega^2 - i\Gamma_j\omega}$$

(4.6)

where the response is summed over \( j \) free electrons, with \( A_j \) relating the strength of the \( j \)-th process with such physical quantities like oscillator strength, and \( \omega_j \) and \( \Gamma_j \) its natural frequency and damping constant respectively [136, 137]. In case of driving a resonance between the atomic levels, \( \omega_j \) takes a meaning of the energy between the levels. Owing to the fact that it arises from a very general and common process of driving of a harmonic oscillator, the Lorentzian lineshape is commonly used to approximately analyze the optical data in a broad frequency range covering different types of excitations.

4.5.2 Resonant Raman scattering

Simple measurements of optical reflectivity or absorption of a sample can reveal only lattice excitations with odd parity which involve a dipole moment and are activated using photon absorption by an oscillator corresponding to the electric-dipole active excitation. In a complementary fashion, even-parity modes can then be revealed using inelastic light scattering, especially using Raman process. In crystals possessing an inversion symmetry, the modes are purely even or purely odd, so none of the excitation can be seen in both IR absorption and Raman scattering channels. In non-centrosymmetric crystals this exclusivity does not take place due to the mixed character of the modes. In general, Raman process may happen not only involving excitations of the lattice, but may involve also spin excitations, as well as can be triggered by a spatial modulation with a finite \( q \)-vector already existing in a crystal. It should be mentioned that in some crystals there are present also silent modes which are not visible via either IR spectroscopy or Raman scattering.

The Raman process may be understood as follows in the semi-classical treatment. The excitations modulate the wavefunctions and energy levels in a solid, which macroscopically corresponds to modification of a dielectric susceptibility tensor \( \chi \). In a general approach, this tensor can be modified by the atomic positions or the electric fields associated with the excitation. One can therefore Taylor-expand the susceptibility as
a function of a normal mode coordinate or as a function of the electric field. The corresponding susceptibility derivatives $\frac{\partial \chi}{\partial Q}$ or $\frac{\partial \chi}{\partial E}$, obtained in such way, are referred to as the Raman tensors of particular order [24, 138]. The time dependent polarization induced by the modulation of susceptibility is regarded as the source of inelastically scattered radiation.

In a way, the Raman scattering can be regarded as a form of modulation spectroscopy, where the excitation itself is the parameter modulating the optical property of a sample [139]. In reflectivity, if $Q$ is the normal mode coordinate, presence of an excitation leads to a modulation of reflectivity $\Delta R \propto \langle \frac{\partial \chi}{\partial Q} \rangle Q$ [140]. This makes the optical reflectivity a good probe of the coherently excited Raman phonons.

The form of Raman tensors for a mode of given symmetry is strictly dependent on the point group symmetry of the crystal. By using a particular light polarization and scattering geometry, one can experimentally “isolate” a certain component of the Raman tensor [24, 138].

The changing intensity of Raman scattering signal seen upon approaching the optical resonance can be understood taking into account the following. Quantum-mechanically, the Raman process corresponds to the absorption of light and excitation of the system from a ground state to a virtual excited state and back to the ground state, with simultaneous emission or absorption of a phonon. Within the third order time-dependent perturbation theory, the Raman tensor for an excitation can be obtained as a sum of terms of a form [139]:

$$\frac{<0|p|1><1|H_{ep}|2><2|p|0>}{(\omega_1 - \omega)(\omega_2 - \omega + \Omega)}$$

Here $|0\rangle$ is the initial state, $|1\rangle$ and $|2\rangle$ are the intermediate states with the energies above the ground state corresponding to $\omega_1$ and $\omega_2$, and this formulation does not include the decay terms of either. The $p$ is the momentum operator and $H_{ep}$ a Hamiltonian describing the electron-phonon interaction. When both intermediate states are taken to be the same, it gives the contribution to the “two-band” Raman process. Otherwise it corresponds to a “three-band” process.

The resonant denominator makes the Raman tensor components to be greatly enhanced when the energy of the incident photon is resonant with the optical gap of the material. In particular, when the energy of the incident photon matches with the smallest energy gap of the system, the biggest enhancement happens to the term which takes the initial state at the upper valence band and the final state at the lower conduction band [138]. Only particular excitations will couple to these electronic levels and so such a measurement helps in determining which phonons have the biggest influence on the band levels involved in the transition activated by the incident light. By analogy, other excitations may be more strongly enhanced when probed with light resonant with other features in optical spectrum.
Apart from giving this kind of information, resonant Raman scattering is in general a useful tool for visualizing excitations that would have been otherwise very weak. Additionally, the resonant enhancement can be so large that it makes visible new types of phenomena, such as multiple scattering by an excitation or scattering from forbidden excitations \[138\].

### 4.6 Coherent excitations

In a time-resolved experiment, in order to see an oscillation in time of a physical variable corresponding to a particular mode, there needs to be a macroscopic coherent change of this observable, related to the excitation. Thermally activated excitations (phonons, magnons...) in a crystal are incoherent with each other in the same fashion as the photons coming out of a thermal light source. However, one can use pulsed light sources to trigger excitations corresponding to the coherent states of the lattice or other long-range-ordered degree of freedom. Such process leads to a macroscopic population of a given mode, and excited quasiparticles correspond to the waves with the same phase across the excited volume. In literature, these are commonly termed coherent phonons, magnons etc.

The process of detection of coherent excitations is in general in a way decoupled from the excitation mechanism. For example, for phonons which are simultaneously Raman and IR-active, the excitation can be done in a resonant fashion, while the probe can employ the Raman scattering effect \[115\]. Both resonantly and non-resonantly driven excitations can be visualized using x-ray diffraction. However, in case of probing reflectivity or transmission, the Raman tensors describing the generation and detection process are both probed in an entangled fashion \[141\]. In case of below-gap excitations where the two-band processes dominate, the amplitude of the time-dependent oscillation should be proportional to the spontaneous Raman scattering intensity \[142\], but in case of probing across the resonance, the spectral dependence of the oscillation amplitude is not directly corresponding to the spontaneous resonant Raman cross-section and therefore to the structure of optical absorption features \[141\].

The section below discusses the ways to generate coherent excitations. In Chapter 5 we perform a resonant excitation of an electromagnon, while in Chapter 7 we observe that the pump pulse creates a population of coherent phonons, and their detected amplitude depends on the probe wavelength.

#### 4.6.1 Resonant excitation of a dipole-active mode

For an excitation possessing a finite dipole moment, an easy way to generate a coherent population is to excite it resonantly with an oscillating electromagnetic wave. The oscillating electric or magnetic field with the right frequency is being absorbed by the excitation, creating a coherent phonon or magnon. Phenomenologically this can
be modeled by assuming that the driving force is proportional to the applied field and the excitation is a damped oscillator. The coordinate of the oscillator corresponds then to the mode coordinate.

Particularly interesting is the scenario when the driving force is so strong that it drives the mode coordinate to the region of potential energy well which is no longer accurately described by the harmonic approximation, and may even drive the coordinate across the potential barrier to another meta-stable equilibrium [3]. This however requires light pulses in the mid-IR/THz regime with extremely high field amplitudes, the generation of which is currently barely at the reach of the experimental capability.

Nevertheless, a big advantage of this technique is that it involves a very efficient energy transfer from the laser pulse to the phonon that changes the mode coordinate. Therefore it is a very promising technique to achieve coherent control over properties of the sample.

4.6.2 Excitation of a Raman-active mode

In order to excite a mode which is not dipole active, but exhibits a Raman activity, a different scheme may be used. When the pulse length is shorter than the period of the vibration, the excitation can be activated using an impulsive stimulated Raman mechanism. Its driving force is no longer simply an electric or magnetic field component of light, but instead it arises from the change of the electromagnetic energy density and so is proportional to derivative of the susceptibility and to the square of electric field [142].

In general, the photon excites the electronic states, which relax very quickly. If afterwards there is no transient deformation of the potential energy landscape of the ions, the force exerted on the ions has an impulsive character, and the induced oscillation of the mode coordinate has a phase shift corresponding to the sinusoidal oscillation. This is the case of transparent materials, where the photons couple only to the virtual excited state.

In the displacive limit, relevant for absorbing materials while the incident light has the energy bigger than the energy gap in the system, the photon excitation corresponds to a redistribution or shift of charges in the unit cell, when the electrons are promoted to a different band. The ions in the crystal suddenly find themselves in a new energy landscape with the energy minima of the excited state located in different position configurations than in the ground state. Therefore the ions start to move and oscillate along the new transient equilibrium. Because their motion is started from a non-zero displacement in the new energy landscape, the oscillation of the mode coordinate has a phase corresponding to the cosinusoidal oscillation.

Detailed analysis [141] points out that the tensor which couples the light to the deformation of the potential, creating the force for moving the ions, and the tensor relating
the ionic motion to the modulation of the susceptibility are not the same. In case of transparent materials, it is only the real part of both tensors which acts in the equation, which is identical for both of them. However in case of absorbing materials, the imaginary parts of the tensors start to play a role, and these are not equivalent. This mechanism is translated into the distinction between the impulsive and displacive limits of the transient stimulated Raman process, and the ratio between the real and imaginary part of the excitation tensor determines the phase of the excited phonon.

These considerations lead to the following summary. When the pump pulse has the energy below the band gap, the main excitation mechanism corresponds to the impulsive force, and it corresponds to the non-resonant Raman scattering involving transitions to virtual excited states in the static case. When the pump pulse is within or above the electronic transition, the force takes a displacive character as it starts to drive the ions towards new equilibrium position. This corresponds to the resonant Raman scattering in the static case.

For most of the cases, the dominating term will correspond to the two-band scenario. Apart from the transient stimulated Raman excitation scheme, coherent phonons may be triggered in a multi-step process, for example by coupling to pump-induced strain or screening field, or by coupling to other coherent modes activated directly by the pump. It should be noted that in the non-resonant methods, the transfer of energy between the pump pulse and the amplitude of the mode coordinate is not as efficient as it is for the resonant methods. Probing of the anharmonic regime is often not possible, because the pump pulse may reach the energies bigger than the damage threshold of the sample before the amplitude of the excited mode becomes big enough.

4.7 Sample preparation

The samples were provided by Dr. S. Koohpayeh from Johns Hopkins University. High quality, stoichiometric TbMnO$_3$ single crystals were grown by the optical floating zone technique at the zoning rate of 0.5 mm/h with rotation rate of 15 rpm for the growing crystal and 0 rpm for the feed rod under static argon.

The crystals were oriented using Laue backscattering and cut to expose the (010) face. The surface of the sample was polished using diamond particles and chemical polishing solution to obtain surface of optical quality. Afterwards the sample was annealed in air in 650°C for 110 h. The dimensions of the crystals are approximately 2 mm × 2 mm × 3 mm.
Chapter 5

Large-amplitude spin dynamics driven by a THz pulse in resonance with an electromagnon

5.1 Introduction

As can be concluded from Chapter 2, type-II multiferroics are materials with a big potential for applications due to the fact that the ferroic orders influence each other. One of the particularly tempting routes towards multiferroic control of material properties is to use electric field in order to manipulate magnetic structure. This can have potential impact for the data storage devices. Currently data storage devices based on ferromagnetic or ferroelectric materials depend strongly on domain reorientation, a process that typically occurs over time scales of several nanoseconds. In case of magnetic storage, head size and the field uniformity pose some limitation on the domain size, and quasi-static domain reversal process relies on the mechanisms not directly related to microscopic material properties. This challenge can be addressed from different perspectives.

The first solution could be to use a multiferroic material in which the information will still be written in the magnetic state but using an electric field. Electric fields are easier to generate and control and allow for more compact sizes. As discussed in previous chapters, TbMnO$_3$ is a well known representative of group of multiferroics exhibiting strong ME coupling, which are a natural first candidate to investigate pathways of multiferroic domain switching. A limitation is, however, that the ultimate speed of control via magnetoelastic coupling remains largely unexplored. First time-resolved measurements on these materials have shown that the speed of domain switching triggered by simple step-function-like electric fields appears to be limited to a timescale of several milliseconds [64]. This would strongly limit the possibility of application of multiferroics. The question arises, can we manipulate the multiferroic degrees of freedom faster
5.2 Experimental setup

than this, and what is the physical limit of speed of such manipulations.

The second solution is to look for a technique which involves a different means to
induce domain state change. For example, there is a big interest in novel ways to
manipulate the magnetic (and other ferro-ordered) domains, especially using laser pulses
[117]. It has been already shown that fast reorientation dynamics may be achievable
using intense electromagnetic pulses [143]. Such pulses can couple to magnetism either
indirectly via electronic excitations [117] or directly via the Zeeman torque induced by
the magnetic field [113, 114, 144]. Direct excitation has the advantage of minimal excess
heat deposition, but requires frequencies in the $10^{10}$–$10^{12}$ Hz range. The low magnetic
field strength of currently realizable THz frequency sources poses a formidable challenge
for such schemes.

In case of multiferroics, optical pulses has been used to affect their magnetic structure
on a femto- and picosecond timescale [95, 108, 111, 145]. Up to now, all the ultrafast
experiments were conducted using indirect pathways to change the magnetic properties
of a multiferroic. It has been predicted that ultrafast magnetic dynamics can be also
triggered by coherent excitation of electromagnons, which are directly connected to
the magnetoelectric coupling [87]. As discussed in chapter 2, in TbMnO$_3$ electric field
of the THz pulse effectively modifies the nearest neighbor exchange constant between
the Mn-spins within the $(ab)$-plane. Monte-Carlo calculations show that for high enough
amplitudes (on the order of 15 MV/cm), the magnetic system undergoes a transition
to a state with different crystallographical orientation of the spin-cycloid plane [87].
Therefore, intense excitation of the zone-edge electromagnon may lead to a picosecond
multiferroic domain switching.

In the following chapter we describe a THz pump–soft x-ray experiment, addressing
the above questions. We investigate whether excitation of electromagnons in TbMnO$_3$
is a viable route for magnetic order control. Our experiment looks at the timescales of
how fast the coupled orders in a multiferroic can possibly respond. Additionally, it takes
into consideration what are the experimental conditions needed to potentially achieve
the switching. We seek an answer whether it is possible to use coherent excitation of
an electromagnon as a means to manipulate the magnetic order, and if yes, what are
the timescales of this process and what is the order of magnitude of the field needed.

The text of this chapter is based on a published paper by T. Kubacka et al. [146].

5.2 Experimental setup

Fig. 5.1 shows a schematic of our experiment. As a pump, we used an intense THz
pulse resonant with the electromagnon frequency. We generated few-cycle, phase stable
THz pulses with a center frequency of 1.8 THz using optical rectification in a nonlinear
organic crystal with a peak electric field of approximately 300 kV/cm at focus [122]. To
see the spin motion resulting from the excitation we used time-resolved resonant soft
Large-amplitude spin dynamics driven by a THz pulse in resonance with an electromagnon

Figure 5.1: Schematic of the experiment. A THz pulse resonant with the strongest electromagnon (lower right inset [85]) excites spin motion in the sample. An x-ray pulse resonant with the Mn $L_2$ edge (upper inset) measures the response as changes in the intensity of the $(0q0)$ diffraction peak (lower left inset). From [146]. Reprinted with permission from AAAS.

x-ray diffraction at the Mn $L_2$ edge and measured the intensity of the first order $(0 q 0)$ cycloid reflection. To achieve the best sensitivity to the signal, we used a single crystal of TbMnO$_3$ cut to expose the $(010)$ surface, and oriented so that the $a$ axis is at $45^\circ$ with respect to the horizontal scattering plane.

The experimental details, such as geometry of the pump–probe setup, procedure used to find overlap between all the beams used, and further insight into the THz part of the experiment, are given in the Appendix A, alongside with the details of data treatment.

5.3 Results

The spin dynamics can be extracted from the behavior of the intensity of the $(0q0)$ diffraction peak as a function of pump–probe delay time $\Delta \tau$. Main experimental results are presented in Fig. 5.2.

At $T = 13$ K, where TbMnO$_3$ is deep in the multiferroic phase, the x-ray signal shows oscillations resembling the shape of the THz pump pulse electric field (Fig. 5.2A). The Fourier transform of the x-ray trace (Fig. 5.2D) shows that the material response has essentially the same frequency spectrum as both the pump and the electromagnon. The delay between the first maximum of the pump trace and the first maximum of the x-ray trace is 250 fs, corresponding to approximately half of a single oscillation
5.3 Results

Figure 5.2: The magnetic diffraction intensity of the (0 $q$ 0) peak of TbMnO$_3$ (blue symbols, left axis), compared with the pump trace (red solid line, right axis) as a function of the time delay. (A, B) The response of the crystal in the multiferroic phase ($T = 13$ K) for opposite signs of the driving electric field. The solid black lines are based on a model discussed in the text. (C) The response in the SDW phase ($T = 30$ K). (D) Fourier transform of the THz and x-ray traces from (A). From [1-46]. Reprinted with permission from AAAS.
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Inverting the sign of the electric field of the pump pulse results in an opposite sign of changes in the diffraction intensity transients (Fig. 5.2B). Such behavior is expected when it is the electric field, and not simple heating, that drives the spin motion.

When TbMnO$_3$ is in the non-multiferroic SDW phase ($T = 30$ K), the oscillation in the peak intensity following the pump is strongly suppressed (Fig. 5.2C). This temperature dependence gives strong evidence that the THz-induced spin motion is correlated with the presence of multiferroicity. At 30 K we tentatively attribute the slight drop of overall intensity after the pump to heating effects from absorption of the THz pulse, which leads to an estimated temperature increase of less than 0.05 K, calculated assuming that all the energy of the incident THz pulse is absorbed by the sample and converted to heat. We used material properties given in a literature [17, 85, 90].

5.4 Modeling

First, we distinguish between the off- and on-resonance excitation scenario by calculating the response of a damped harmonic oscillator driven with the force proportional to the amplitude of the electric field of the THz pump pulse, and by assessing the magnitude of the response of the sample in case of purely magnetic excitation.

Second, we build a numerical model of an equilibrium magnetic structure as seen by resonant x-ray diffraction, basing on the data collected in the static experiment at a synchrotron. We then distort the spin directions following two spin motion patterns predicted by theory and recalculate corresponding diffraction intensity changes, in order to distinguish between different spin motion patterns potentially contributing to our signal.

Third, we quantitatively estimate the amplitude of the spin motion by comparing the time-dependent diffraction intensity modulation with the corresponding change of magnetic structure in equilibrium conditions.

5.4.1 Off- and on-resonance excitation

Electromagnon as a driven harmonic oscillator To better understand the time dependence of the spin response, we construct a very simple model of the system as two independent simple harmonic oscillators at the electromagnon resonance frequencies of 0.7 THz and 1.8 THz.

Let $q_1$ and $p_1$ be the “position” and “momentum” canonical coordinates for the lower energy oscillator. Similarly, let $q_2$ and $p_2$ be the canonical coordinates for the higher energy oscillator. The full dynamics are then given by a system of four first order ordinary differential equations

$$\frac{dq_j}{dt} = p_j$$
\[ \frac{dp_j}{dt} = f_j(t) - 4\pi \zeta_j \nu_j p_j - 4\pi^2 \nu_j^2 q_j \]

where \( \nu_j \) and \( \zeta_j \) are the natural frequency and damping for each oscillator, and \( f_j(t) \) is the driving force which we assume here is proportional to the electric field of the applied THz pulse. The solutions in the Fourier domain are

\[ Q_j(\nu) = \frac{F_j(\nu)}{4\pi^2 (\nu_j^2 - \nu^2 - 2i\zeta_j \nu_j \nu)} \]

\[ P_j(\nu) = \frac{i\nu F_j(\nu)}{2\pi (\nu_j^2 - \nu^2 - 2i\zeta_j \nu_j \nu)} \]

where \( Q_j, P_j \) and \( F_j \) denote the Fourier transforms of \( q_j, p_j \) and \( f_j \). Since the imaginary part of the dielectric permittivity \( \varepsilon \) is proportional to a weighted sum of the imaginary parts of \( Q_1(\nu) \) and \( Q_2(\nu) \), we can use the published permittivity data [85] to estimate \( \nu_1 = 0.75 \) THz, \( \nu_2 = 1.85 \) THz, \( \zeta_1 = 0.34 \) and \( \zeta_2 = 0.198 \). The resulting fit is shown in Fig. 5.3A.

Upon inverse Fourier transform, we can then compare our model, one mode at a time, with the recorded time-domain material response. In Figs. 5.3B and C we plot both \( q_j(t) \) and \( p_j(t) \) for each oscillator. These curves are each scaled by a constant, adjusted individually to best match the data. For \( p_1 \) and \( p_2 \) the scaling constants are negative, an allowance for the ambiguity in the absolute sign of the effective force on the oscillator. These scaling factors are the only adjustable fit parameters in the model.

As seen in Fig. 5.3B, \( p_2(t) \) fits the data reasonably well, recovering the correct phase delay between the pump and observed x-ray oscillation. Neither \( q_1(t) \) nor \( p_1(t) \) reproduce the experimental data well, both reacting significantly earlier in time than the measured spin response. The “delay” with response to the driving field observed in the data is in fact a direct consequence of driving the oscillator in resonance. In resonance, energy is efficiently transferred to the oscillator and stored there until the natural damping effects lead to a decay of the coherent response.

To sum up, although not a perfect match to the data, the behavior of the conjugate momentum of the higher frequency oscillator successfully reproduces the general shape of the oscillation and the delay between the driving electric field and the changes in x-ray diffraction (Fig. 5.2A and B). The agreement is much worse for either canonical coordinate of the lower frequency oscillator, suggesting that off-resonant excitation of the lower energy electromagnon or other purely magnetic modes is not consistent with the measured shape or delay of the response. When “position” of the oscillator corresponds to a magnetization along one direction, we can identify the “momentum” of the oscillator as a magnetization component along another axis, meaning that in our experiment we are sensitive to the conjugate motion of the spins.
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Figure 5.3: (A) Measured Im[\varepsilon] from ref. [85] compared to the fitted results from the model discussed in the text. (B) The simulated responses of the 1.85 THz mode. (C) The simulated responses of the 0.75 THz mode. In each plot red is the electro-optic THz trace, blue circles indicate the measured response, and the calculated responses \( q_j(t) \) and \( p_j(t) \) are shown as dashed and solid lines, respectively. The amplitudes of the simulated responses are individually scaled to best match the experimental data. From [146]. Reprinted with permission from AAAS.
5.4 Modeling

Estimate of magnetic-field induced dynamics  To estimate the maximal effect of the non-resonant oscillating magnetic field component of the THz excitation on the observed x-ray diffraction, we consider the unconstrained precession of the spin magnetic moments $S_i$ given by

$$\frac{dS_i}{dt} = -\gamma S_i \times B(t)$$

where $B(t) = B_0 \ g(t)$ is the applied magnetic field, $\gamma = 1.76 \cdot 10^{11}$ rad/T·s is the gyromagnetic ratio, $B_0$ is the magnitude and direction of the magnetic field, and $g(t)$ gives its time dependence. Assuming the changes in spin direction are small, to leading order we integrate to obtain

$$S_i(t) \approx S_i^0 - \gamma S_i^0 \times B_0 \int_{t_s}^{t} g(t') dt'$$

where $S_i^0$ is the initial spin orientation at a time $t_s$ well before the THz pulse interacts with the system. Since this relation is linear in $S_i^0$ and the Fourier transform of the spin density is also a linear operation, the time-dependent magnetic structure factor $f_{0q0}(t)$ has the same form

$$f_{0q0}(t) \approx f_{0q0}^0 - \gamma f_{0q0}^0 \times B_0 \int_{t_s}^{t} g(t') dt'$$

Using the value of the magnetic structure factor $f_{0q0}^0$ inferred from the equilibrium measurements, we then calculate the effect on the diffracted intensity [147]. For the 0.1 T peak fields used in our experiment we estimate a maximum change in the diffracted intensity of 0.035%, well below the modulations we observe. This supports our understanding that the signal we see is not the effect of the magnetic field driving the spins off-resonantly.

5.4.2 Assignment of spin motion patterns

As discussed in Chapter 4, resonant x-ray scattering at the Mn $L$-edge is predominantly sensitive to the magnetic moment of the Mn 3$d$ shell [131]. An analysis of how different spin motions contribute to the intensity of the diffraction peak allows us to test which of them are involved in the observed oscillations.

We consider two components of the induced spin motion, motivated by the current understanding of spin dynamics in this system. In the first component the spins move in antiphase within the spin cycloid plane, the pattern widely considered to be responsible for the infrared activity of the 1.8 THz electromagnon [83] (cf. 2.6). The driving electric field applies an effective “force” to this component. In our model of the electromagnon as a harmonic oscillator, this component of the spin motion should then be identified with the “position” of the oscillator. In the proposed pure spin Hamiltonian for this system [87], the conjugate momentum must be a spin motion orthogonal to this position coordinate. Numerical simulations based on this Hamiltonian have predicted that a sufficiently intense THz pulse in resonance with the 1.8 THz electromagnon can induce...
Large-amplitude spin dynamics driven by a THz pulse in resonance with an electromagnon

Figure 5.4: Spin-motion patterns analyzed to interpret the time-dependent data. The upper panels illustrate the different patterns of how the magnetic structure changes. Black arrows denote how the spins are oriented in the ground state. Color arrows indicate the spin directions at one of the extremes of the excited motion. Tb ions have been removed for clarity. The lower panels show calculations of the changes in $(0q0)$ peak intensity as a function of the motion coordinate. (A) Antiphase oscillation within the spin cycloid plane, parameterized using the spin rotation coordinate $\varphi$ and viewed along the $a$ axis. (B) Coherent rotation of the spin cycloid plane by an angle $\varphi'$ about the crystallographic $b$ axis viewed along the $b$ axis. From [146]. Reprinted with permission from AAAS.

coherent rotation of the spin cycloid plane about the $b$ axis until it reaches another stable orientation in either the $(ab)$- or $(bc)$-plane [87]. In our experiment the effective THz pulse field strength is over two orders of magnitude lower than used in these simulations and so we do not expect to see a persistent domain reorientation. Instead, we propose to consider a smaller rotation of the spin cycloid plane about the $b$ axis as a second component of the spin motion that corresponds to the conjugate momentum for the 1.8 THz resonance.

We model these two spin motion patterns separately as distortions to the equilibrium magnetic structure which influence the magnetic structure factor. We then calculate the intensity of the $(0 q 0)$ diffraction peak as a function of each coordinate of the spin motion (Fig. 5.4).
5.4 Modeling

Figure 5.5: Dependence of the (0q0) diffraction peak intensity on the azimuthal angle for the π- and σ-polarized incident x-rays (filled black and open red symbols, respectively), without outgoing x-ray polarization analysis. The azimuthal angle is defined to be zero when the a axis is in the horizontal plane. Solid lines show the fit to the data. The uncertainties are smaller than the symbol size. From [146]. Reprinted with permission from AAAS.

In order to be able to reconstruct the magnetic diffraction model, we analyze the azimuthal scan of the (0 q 0) peak at the Mn L$_2$ edge measured in a separate experiment at the RESOXS endstation at the SIM beamline (Swiss Light Source, PSI) [148] for π- and σ-polarized incident x-rays without the analysis of the diffracted beam polarization (Fig. 5.5) [149]. The calculation of the Fourier coefficients of the magnetic structure of TbMnO$_3$ in the multiferroic phase contributing to the (0 q 0) peak visible in the resonant scattering experiment is performed using the program BasIreps 4.10 included in the FULLPROF suite. In the multiferroic phase two irreducible representations are required to describe the magnetic structure [18]. The values of the components of the basis functions along the b and c axes are obtained from the fit to the experimental data (solid lines in Fig. 5.5). For the magnetic structure factor of a form $f_{0q0} = (0, v, w)$ we obtain $v = 0.57i$ and $w = 1$. The directions and amplitudes of the contributions of magnetic moments visible in the experiment are then calculated from the Fourier coefficients. Our data are consistent with the cycloid propagating along the b axis, and the Mn spin components along the c axis we observe at this particular reflection are ordered ferromagnetically along the c axis, consistent with the scenario proposed by [101]. The resonant x-ray diffracted intensity and the shape of the azimuthal scans are calculated numerically following [147, 150] confirming a good agreement with the experimental data.

In the next step, the magnetic structure is deformed by rotating the spins on particular sites by an angle ±φ (±φ′), in order to reproduce the magnetic structure during the spin excitation in a state “frozen” in time. For every φ (φ′), we compute the magnetic structure factor of the resulting distorted magnetic structure. The intensity of the (0 q 0) diffraction peak at azimuth of 45° and π-polarized incident x-rays is then calculated and normalized to the value obtained for φ=0 (φ′=0) (the case of non-distorted cycloid).
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The results of the modeling are shown in Fig. 5.4. For the in-plane motion the intensity of the diffraction peak is an even function of the spin coordinate, giving a decrease of the diffracted intensity with twice the frequency of the spin motion (Fig. 5.4A). Similar result was obtained for other AFM-type patterns, including the AFM-type cycloid plane rotation. For the spin cycloid plane rotation consistent with the motion leading to the coherent flop of the cycloid plane, the change of diffracted intensity is an odd function of the rotation angle. This motion then leads to a modulation of the diffraction intensity with the same frequency as the spin motion (Fig. 5.4B). For a field-driven excitation process we expect the spin motion frequency to be the same as the frequency of THz pump. We conclude that the main motion visible in our experiment is a rotation of the spin cycloid plane. The in-plane spin motion may also be present, but its response would be suppressed at the current experimental time resolution. This is consistent with our harmonic oscillator model, which suggests that we see primarily dynamics of the conjugate momentum of the resonance.

5.4.3 Calculation of the tilt angle of the cycloid

For π-polarized x-rays at the Mn $L_2$ edge the scattering intensity is a strongly varying function of the sample azimuth (rotation about the Bragg wave vector). Rotation of the spin cycloid plane about the $b$ axis induced by the THz pulse is equivalent to rotating the sample about the $(0 \ q \ 0)$ scattering vector. Hence we interpret the data quantitatively by comparing the change of the intensity of the diffraction peak seen in the pump–probe trace with the change corresponding to rotating the sample by a small angle around the azimuth of 45° in equilibrium conditions (Fig. 5.6). We estimate that the observed (1.35±0.12)% maximum change of peak intensity corresponds to an amplitude of spin cycloid plane rotation equal to (4.2±0.4)°. We expect higher fields will lead to larger spin cycloid rotations. A simple linear extrapolation suggests that THz pulses with an amplitude of 1–2 MV/cm inside the sample could lead to spin cycloid rotations on the order of 90°. We can compare this against the model of [87], which predicts switching at 14–15 MV/cm for single-cycle THz pulses.

5.5 Conclusions

Out of our measurement, we can take the following conclusions.

First, we demonstrate that the magnetic structure of multiferroics can respond within a fraction of a picosecond after the excitation. It is far above the previously established limit of several milliseconds and suggests a way to achieve ultrafast heatless multiferroic domain switching. Given that TbMnO$_3$ is a model compound for a large group of materials with noncollinear spin order, our results serve as a proof-of-principle for a wide range of compounds. Moreover, the presence of magnetoelectric coupling in multiferroic
5.5 Conclusions

Figure 5.6: The diffracted intensity vs. spin cycloid rotations. Left: Azimuthal dependence of the \((0q0)\) peak for the \(\pi\)-polarized incident x-rays divided by the diffracted intensity at an azimuth of 45°. Right: Time-resolved diffracted intensity normalized to the intensity before excitation. The blue plane represents a plane of a single spin cycloid propagating along the crystallographic \(b\) axis. The \(a\) axis is marked with red. The angles of rotation in the drawing have been exaggerated for clarity. From [146]. Reprinted with permission from AAAS.

heterostructures encourages a search for similar mechanisms as a basis for technologically feasible multiferroic devices.

Second, we directly visualize the spin motion associated with the excitation of the electromagnon and compare it with previous predictions based on spectroscopic data. In a current experimental setting we are not sensitive to the motion of spins predicted to be dominant for the zone-edge electromagnon (cf. 2.6). Instead, we see a rotation of a cycloid about its propagation axis, which is a first step towards coherent flop of the cycloid plane predicted by numerical simulations.

Furthermore, we quantitatively determine the amplitude of the spin motion, and estimate that the field of 65 kV/cm inside the sample and along the sensitive \(a\) axis leads to rotation of approximately 4°. We estimate that in order to achieve the switching, we would have to deal with the fields on the order of 1–2 MV/cm inside the sample.

An open question is still a more exact determination of the motion pattern of the spins involved in the electromagnon. Given the ambiguity of the assignment of the \(k\)-vector coming from the neutron measurements, a time-resolved resonant x-ray scattering experiment at additional magnetic satellites, sensitive to different Fourier components of magnetic structure, could help to solve this puzzle. Additionally, we discover that the the simple prediction of the spin motion pattern from the linear spin-wave theory would not lead to a signal observed by us. This points to a potentially richer physics behind the electromagnon generation. By measuring the response of the equivalent (Eu,Y) solid solution, one could separate the influence of the \(4f\) spins on the observed dynamics. Last, a measurement of the lattice distortions associated with the electromagnon excitation would be an interesting confirmation of its microscopic origin.
Chapter 6

Direct visualization of demagnetization dynamics of optically pumped TbMnO$_3$

6.1 Introduction

The previous chapter concentrated on manipulation of magnetic order in a non-thermal fashion, making use of resonant excitation of an electromagnon. It is however interesting to look also at the magnetization dynamics of a spin-cycloid multiferroic triggered by an optical pulse, which couples to the properties of the crystal in an entirely different fashion.

In $d^4$ manganites, the excitation mechanism upon using a 1.55 eV pump has been proposed to involve creation of the Mn$^{2+}$Mn$^{4+}$ pairs [108]. As discussed in Chapter 1, none of the excited manganese ions is Jahn–Teller active, which leads to creation of the AJT polarons with locally undistorted MnO$_6$ octahedra. Due to the fact that the polarons are embedded in the network of collectively rotated, strongly JT-active octahedra, they are strongly pinned to the lattice which hinders hopping processes. The creation of the AJT polarons is therefore a process in which the electrons, spins and lattice are intrinsically coupled.

It has been shown that the creation of the AJT polarons in manganites is accompanied with excitation of coherent phonons coupled to the particular undistortion pattern [4, 8]. The polarons are created in both paramagnetic and magnetically ordered state, and it has been shown that in the A-type LaMnO$_3$ the presence of long-range magnetic correlations influences the damping process of the coherent phonons [8].

In spin-cycloid manganites, the process of polaron creation may be more strongly connected to the magnetic structure. This is due to the fact that the nearest neighbors are never aligned ferromagnetically, as the pure FM ordering along $a$-axis only concerns...
6.2 Scattering off the (0 q 0) and (0 2q 0) diffraction peaks

the next-nearest-neighbors. This is in contrast to the pure A-type ordering seen in $\text{RMnO}_3$ with bigger ionic radius. In spin-cycloid manganites the Mn–O–Mn bonds are aligned diagonally to the FM-$a$-axis and cycloid-$b$-axis, and the nearest neighboring manganese spins are always canted in respect to each other by $360^\circ - (q/2)$ within the $(ab)$-plane. This can potentially influence the mechanism of polaron creation and relaxation.

It has been shown in the optical pump–probe experiments looking at the optical reflectivity that the excitation with a pulse mainly resonant with the $d$–$d$ transition feature induces changes to the magnetic structure of spin-cycloid multiferroics [95, 108] on the timescale of several picoseconds. None of these experiments however unambiguously untangled the magnetic information from the influence of other degrees of freedom, as physical processes coming from magnetic, lattice and electronic subsystems simultaneously contribute to the optical properties of solids. The resonant x-ray diffraction has the advantage of looking upon magnetization in a direct way and can remove the ambiguity of the optical results. Additionally, while the optical probe is sensitive mostly to the short-range spin spin correlations [16], the x-ray diffraction gives complementary information about the long-range spin correlations.

This chapter presents results of two experiments, which look directly at the ultrafast destruction of magnetic order in TbMnO$_3$ upon excitation with the pump pulse with 1.55 eV photon energy.

In order to gain understanding of the physical processes contributing to the probe signal, the results of pump–probe experiments are preceded with the brief discussion of the temperature and polarization dependence of chosen diffraction peaks, measured in separate experiment in equilibrium conditions.

The first time-resolved experiment investigates the pump fluence dependence of the demagnetization dynamics. It looks at its relation with the effective spin temperature.

Second experiment takes a closer look at the process of melting of magnetic structure, by separating particular contributions to the scattering by controlling the polarization of the incident x-ray light and looking at different reflections with contributions to the structure factor coming from spins and associated orbital deformations. The effective temperatures and associated melting timescales of particular subsystems are analyzed.

### 6.2 Scattering off the (0 q 0) and (0 2q 0) diffraction peaks

The static data was collected at the RESOXS endstation of the SIM beamline at the Swiss Light Source (PSI) [148]. The (0 q 0) peak was measured at the Mn $L_2$ absorption edge (652 eV) for both $\pi$ and $\sigma$ polarization of incident x-rays, without polarization analysis of the outgoing beam. Within the description and interpretation of the experimental results, we use a symbolic notation of $(0 \ t \ 0)$, where $t = q, 2q$ and $i = \pi, \sigma$ to denote the measurement of the $(0 \ t \ 0)$ peak with $i$-polarized incident x-ray beam. The sample was $b$-cut and placed at azimuth of 0° ($a$-axis in the scatter-
Direct visualization of demagnetization dynamics of optically pumped TbMnO$_3$ing plane). The measurement was performed by Y. W. Windsor, E. M. Bothschafter, L. Rettig, M. Ramakrishnan, A. Alberca and U. Staub.

The results for (0 $q$ 0) and (0 2$q$ 0) peaks are summarized in Fig. 6.1. As discussed in [101] and Chapter 3, the magnetic satellites (0 $t$ 0), where $t = q, 2q$ arise from the F-deformation of the spin cycloid. Its source is the DM interaction, rotating the spins within the ($bc$)-plane out of their positions within the uniform cycloid. This deformation is strongly and intrinsically coupled to the main A-type magnetic ordering of the spin cycloid and conclusions from measurement on this reflection can be extrapolated onto the main cycloid.

The $q$-position of the diffraction peaks for both polarizations shows a similar temperature dependence. In the sinusoidal phase the $q$ decreases with temperature almost linearly, reaching minimum at the multiferroic phase transition. Below $T_C$, both peaks show the same temperature dependence of $q$—after a rise close to the phase transition, below approx. 25 K the $q$ is almost constant with temperature.

The phase transitions are visible in both intensity and position of the (0 $q$ 0) peak. In case of $\pi$ polarization, the peak is visible for $T < T_N$ with a kink at $T_C$, where it seems a second ordering process sets in. The same peak at $\sigma$ polarization only appears at $T_C$ and similarly follows a square-root-like growth in intensity while decreasing temperature.

Compared to the (0 $q$ 0) peak, the intensity (0 2$q$ 0) peak shows a different temperature dependence. Instead of the square-root behavior, with lowering temperature peak intensity rises linearly (Fig. 6.1). Interestingly, in the case of the second harmonic peak, the polarization dependence is inverted, and now it is the $\sigma$ polarization which gives much higher peak intensity than the $\pi$ polarization. Both polarizations see finite intensity already in the SDW phase. When scaled onto each other and normalized to the value at 12 K, it becomes apparent that both polarizations see the same temperature dependence of the (0 2$q$ 0) peak intensity, but with differing amplitudes (Fig. 6.2).

Following the analysis of the magnetic components involved in scattering at this particular azimuth [101, 149, 151], one can better understand different temperature behavior of the measurements with $\pi$ and $\sigma$ polarization.

In the simplest model, when looking at the (0 $q$ 0) peak at this azimuth, $\sigma$ polarized x-rays will be sensitive only to the $c$-axis component of magnetization, and the $c$-axis spin-spin correlations set in only at $T_C$. Contrary, the $\pi$ polarization will see both $b$ and $c$-axis components of magnetic structure, and so it will see finite intensity already in the SDW phase.

The reason for which the $\sigma$-polarized peak is not sensitive to the SDW phase is the easiest to understand in the following way. As follows from the discussion in Chapter 4, the resonant process requires presence of the spin component (and more generally, scattering length tensor) along the electric-field component of the incident x-ray beam (Eq. 4.5). In the SDW phase, in experimental configuration of the sample with the ($ac$)-surface exposed and $a$-axis in the scattering plane, there is no projection of the spin
6.2 Scattering off the \((0 \, q \, 0)\) and \((0 \, 2q \, 0)\) diffraction peaks

Figure 6.1: Temperature dependence of the intensity and position in reciprocal space of magnetic diffraction peaks in TbMnO\(_3\).

Figure 6.2: Peak intensity for both first and second harmonic magnetic reflection, normalized to the value at lowest temperature and offset for the sake of comparison with the pump-probe measurement.
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(collinear and parallel to the $b$ axis) onto the electric field direction, which for the $\sigma$ polarization is pointing perpendicular to the scattering plane. On the contrary, the $\pi$ polarized incident light will see a finite projection of the collinear, $b$-oriented spin, due to the fact that the sample is placed at the Bragg condition and the spins have a finite projection onto the direction of the $\pi$-polarized electric field of incident x-rays. Observed temperature behavior is consistent with the calculations of [20], where the correlations along $b$-axis smoothly increase starting from $T_N$, and the correlations along $c$ set in only at $T_C$ (Fig. 3.3).

While the behavior of the $(0 \ q \ 0)$ peak can be explained reasonably well within the stick model of spin, the origin of the $(0 \ 2q \ 0)$ peak is more complex. It has been shown that it exhibits finite scattering intensity in polarization channels which would have been forbidden if the underlying magnetic order could be well described by the dipole terms only [149].

On one hand, the second harmonic satellites come from the $(e^* \cdot \hat{s})(e \cdot \hat{s})$ terms (Eq. 4.4) [147], and so their structure factors contain the square of the spin $<S^2>$, as opposed to the first harmonic arising from $(e^* \times e) \cdot \hat{s}$ term, and so corresponding to $<S>$. In the first approximation, when the spins in the TbMnO$_3$ crystal are visualized as arrows following a cycloid, in this interpretation the second harmonic peak is sensitive to the directions of the sticks, which changes with twice the spatial frequency, but not to the direction of the arrows themselves. This is however only intuitive approximation not including the additional multipole terms, involved in the scattering, as presence of the quadrupole term destroys the exact correspondence between the $(0 \ 2q \ 0)$ and the $<S^2>$ [149].

The multipole description of the atoms involved in resonant scattering process gives additional insight into microscopic origins of the $(0 \ 2q \ 0)$. In case of the $(0 \ q \ 0)$ involved multipoles correspond to the form of a dipole. The diffracted intensity of the $(0 \ 2q \ 0)$ is thought to arise from the higher rank tensors, corresponding to the quadrupole terms [149]. These are related to the charge asymmetry and can thus be connected to the orbitals affected by the magnetic ordering with twice the incommensurate ordering vector of the main spin cycloid. Having in mind that in general the second harmonic peaks can be associated with the static strain wave accompanying the incommensurate magnetic deformation [90], one could possibly relate the oxygen displacement associated with the IDM interaction to the additional spin rotation due to the action of IDM, and to the local distortion of the orbital via the incommensurate modulation of the Mn–O–Mn bond and thus orbital-mixing angle (cf. Fig. 1.3).

Inspection of formulas given in [149] confirms that the $(0 \ q \ 0)_\sigma$ channel is sensitive purely to the $B_{11}$ multipole, and $(0 \ q \ 0)_\pi$ channel is dominated by the additional scattering off the $A_{10}$ multipole. In the $(0 \ 2q \ 0)_\sigma$ channel dominant contribution comes from the $A_{20}$ multipole, while in the $(0 \ 2q \ 0)_\pi$ channel the contributions of particular multipoles almost cancel out. The theory predicts that the ratio of peak intensities
should be $I_2^q/I_\pi^q \approx 0.1$ and $I_\sigma^q/I_\pi^q \approx 3.7$. This is in good agreement with the experimental observation. Unfortunately in the incommensurately modulated systems there is no immediate correspondence between particular multipoles and dipoles or orbitals [151].

Last, from a different point of view, particular magnetic satellites are related to the certain Fourier components of magnetic structure. The fact that we can see the second harmonic reflection means that the underlying magnetic order cannot be described by a single sinusoidal function.

### 6.3 Magnetic order dynamics in optically excited multiferroic TbMnO$_3$

In order to investigate the demagnetization process in TbMnO$_3$ using a direct probe of magnetism, we performed a 1.55 eV pump–resonant x-ray probe experiment using high pump fluences. The experiment was done at the SXR beamline at Linac Coherent Light Source [152, 153]. The results and analysis reported in this section have been published in paper by J. A. Johnson et al. [154].

#### 6.3.1 Experimental setup

The $b$-cut TbMnO$_3$ sample was oriented so that the $a$-axis was in the horizontal scattering plane, and placed in the Bragg condition to measure the $(0 q 0)$ magnetic diffraction peak. The incident x-ray photon energy was in resonance with the Mn $L_2$ absorption edge (652.5 eV). The Kirkpatrick–Baez optics were used to focus the beam to a spot size with a diameter less than 300 µm. Using the fast charge-coupled-device (fCCD) camera, we measured the $(0 q 0)$ diffraction peak in the in-plane scattering geometry as a function of relative delay between collinear propagating x-ray pulses ($\pi$ polarized; 100 fs FWHM) and 800 nm (1.55 eV) pump pulses (120 fs pulse duration; 140 µm FWHM; $p$-polarized). The laser fluence was controlled using a $\lambda/2$ waveplate and a polarizer. The data are plotted against an absorbed fluence using the optical constant of TbMnO$_3$ referred in [94]. The optical penetration depth at 1.55 eV is no less than 160 nm within the $(ab)$-plane [94], while we estimate the penetration depth of x-rays at the Mn $L_2$ edge for less than 60 nm.

#### 6.3.2 Results

Fig. 6.3 shows the data collected for different pump fluences. All the collected datapoints were binned into 1-ps wide bins, and a 2D Gaussian peak was fitted to the fCCD images, which were processed in the way as described in Appendix A.
Direct visualization of demagnetization dynamics of optically pumped TbMnO$_3$

Figure 6.3: (a) Decay of magnetic diffraction peak intensity over time for different absorbed pump fluences. (b) Change of apparent $q$ as a function of pump fluence. Amplitude (c) and decay time (d) of an exponential fit vs. pump fluence.

The normalized intensity and $q$ of the fitted peak (taken as a position in 2Θ on the fCCD image) are plotted in Fig. 6.3a–b (standard error bars are roughly the size of the symbols). The most pronounced effect is that after pump excitation, the intensity of the peak decays exponentially with time, with the decay rate and decay amplitude increasing with the laser fluence. For times after time-zero, the following model is used to quantify the decay process:

$$I(t)/I_0 = A[\exp(-t/\tau) - 1] + 1$$

(6.1)

Fit amplitudes $A$ and decay time $\tau$ are plotted against fluence in Fig. 6.3c–d. First, the peak nearly vanishes for long delay times for fluences larger than 7 mJ/cm$^2$. The time constants of the decay for fluences below roughly the same threshold value are similar. We estimate the value to be 22.3(1.1) ps. For higher fluences the time constant becomes fluence-dependent, reaching $\sim$7 ps for the highest applied fluence of 18.4 mJ/cm$^2$.

Looking at the time-dependent behavior of the apparent $q$, some shift in $q$ (up to $\Delta q = +0.002$ r.l.u.) can be observed for high fluences. However, the observable $q$ shift happens only for the datapoints where the intensity of the diffraction peak is very low. We attribute this remnant diffraction peak intensity along with the $q$ shift to the fact that our pump and probe sizes were comparable and the probing x-rays would still see a region of the sample which has not absorbed fluence high enough to make the diffraction peak disappear.
6.3 Magnetic order dynamics in optically excited multiferroic TbMnO$_3$

Phenomenologically, we can attribute observed exponential decay to an incoherent melting process, which corresponds to the spin temperature increase. We can estimate the effective spin temperature by comparison with the static temperature dependence of peak intensity for the same x-ray polarization (cf. Fig. 6.1). We can approximate the temperature dependence by a linear fit with the slope of 0.0311(10) [1/K] and offset of 1.39(2) (red line in the inset of Fig. 6.4). Using this fit, the time-resolved intensity can be approximately mapped onto the effective temperature of the spin system. Left panel of Fig. 6.4 shows the evolution of the spin temperature vs. time for different pump fluences, with the symbols representing the experimental data in the range below 35 K ($I(t)/I_0 \approx 0.25$).

Since the diffraction peak vanishes at the Néel temperature, we only have the information about the spin temperature below 42 K, but we expect that higher pump fluences would increase it accordingly more. To get a qualitative insight into this question, we perform a second exponential fitting of the data in Fig. 6.4, assuming that for every pump fluence the underlying decay time relating the speed of the melting is constant and equal to $\tau = 22.3$ ps (the value we obtain for low fluences which do not pump away the peak entirely). We let the effective temperature to be a fitting parameter in the equation

$$T_{\text{spin}}(t > 0) = (T_0 - T_f) \exp(-t/\tau) + T_f$$

where $T_0 = 12$ K is the initial temperature before time-zero and $T_f$ is the effective spin system temperature. We use only the initial part of the experimental curve, in the range of spin temperatures as described above. The results of the fit are shown as solid lines in Fig. 6.4, and the right panel summarizes the $T_f$ as a function of fluence. For the highest fluence, the spins reach temperatures of around 80 K, and they depend linearly on fluence within the majority of the covered fluence range. The spin

Figure 6.4: (a) Mapping of the peak intensity onto the effective spin temperature $T_f$ using the static data (inset) and a fluence dependence of $T_f$ (b).
temperature is directly proportional to some fraction of the absorbed energy of the pump pulse, suggesting a simple coupling process.

6.3.3 Discussion

Following the discussion of optical properties of the manganites, we can identify the main microscopic mechanism following the absorption of 1.55 eV radiation (cf. Fig. 1.11). Although the pump energy does not match exactly the center of the main $d-d$ feature (2 eV), there is still significant absorption due to the relatively broad width of the peak. An additional—much smaller—contribution to the $p-d$ transitions may come from the far wing of the 4 eV and 5.5 eV feature. We discriminate between the two types of transitions by noting that we do not observe a significant increase of the diffraction intensity around time zero. Assuming that the incident pump pulse creates a population of AJT polarons due to the $2\text{Mn}^{3+}\rightarrow\text{Mn}^{2+}+\text{Mn}^{4+}$ process, we do not expect this process to affect the intensity of the diffraction peak directly. This is because the magnetic scattering cross-section effectively relates the average of the square of the spin length $\langle S^2 \rangle$, and this value is conserved upon this excitation. This would not have been the case if the 1.55 eV pump would cause transitions where additional spins would be injected from the oxygen ligands onto the manganese sites. Therefore we assume that the main process following the excitation with 1.55 eV is to cause $d-d$ transitions and create a population of AJT polarons in the crystal.

We note that the timescales we observe are in qualitative agreement with measurements done using purely optical probe [95, 108]. Following this scenario where the major contribution to the dynamics seen in these experiments comes from the short-range spin correlations, we can conclude that the process of demagnetization happens on a similar timescale for both short and long-range spin correlations. The microscopic reason for the long timescales observed remains however unclear, basing only on the results of the x-ray scattering. There are several mechanisms that could explain the relatively long decay time observed.

First, in the measurement on the $(0 \ q \ 0)$ peak we are sensitive to the secondary order parameter, which is arising from the lattice distortions due to the DM mechanism. While in the static case they are strongly coupled to the spin components of the main A-type cycloid [101], in the dynamic case they may relate a contribution to the magnetism which exhibit different – potentially longer – timescale than the main components. To investigate this scenario, the measurement at $(0 \ q \ 1)$ or equivalent reflections or at the structural peak corresponding to the oxygen displacements related to the F-type deformations would be needed.

Second, the AJT polarons couple the electronic excitation, lattice distortion and the spin degree of freedom. If the demagnetization were induced by the magnon-assisted-hopping of excess carriers as proposed by [95], it would have to be assisted by the lattice
6.3 Magnetic order dynamics in optically excited multiferroic TbMnO$_3$

rearrangement, which strongly pins the polarons. Since the process of hopping would
have relatively low probability, it would slow down the demagnetization process. In an
alternative scenario, the picosecond decay time may reflect the lifetime and process of
recombination of the polarons. In case of strong spin correlations and strong lattice
distortion the recombination process would be hindered leading to long decay times
[108].

Third, because no nearest neighbors in spin-cycloid manganites are aligned ferromagnetically, when the incident photon creates a pair of Mn$^{2+}$Mn$^{4+}$ there is an additional
cost associated with rotating the spin of the excited electron so that it is aligned with
the core spin of the accepting site. This process would create a population of magnons
with high momentum. The dynamics we see are coupled to the low-momentum magnetic
excitations and magnetic system may need time to thermalize, so that the energy is
transferred between the high-momentum and low-momentum excitations. Additionally,
the pump-induced magnetic defects will be surrounded by a locally different magnetic
mean field, and the nearest neighbors surrounding the defects will experience a change
of sign of the exchange constant across the bond joining the Mn$^{3+}$ and excited Mn$^{2+}/^{4+}$
ions [8, 108]. The defects may try to reduce the magnetic strain by delocalizing onto their
neighbors and forcing their reorientation, and by driving the precession of other spins,
which leads to incoherent loss of correlation. The processes involving spin precession
are usually characterized by relatively long timescales [117].

Based on the AJT polaron creation mechanism, we can also speculate on the mecha-
nism behind the observed fluence dependence. We can estimate that the fluence on
the order of 7 mJ/cm$^2$ corresponds to roughly one per 10 unit cells absorbing a photon
and so 2 Mn ions out of 40 become JT-undistorted. Given that creation of an AJT
polaron is accompanied with a local strain field, it is not unlikely that the interaction
between the polarons starts to play a role when they are separated by distances compa-
rrable with their own size. The fluence threshold for the linearity of the data observed in
the experiment (Fig. 6.3c–d) may therefore correspond to reaching the polaron density
which is enough for the polarons to become coupled to each other.

Interestingly, we observe that the melting of the cycloid seems to be unaccompanied
by a change in $q$, contrary to how it happens in the static case when the $q$ rises up to
$\Delta q = 0.01$ between $T_N$ and $T_C$. Taking into account the magnon dispersion curve around
the $q = (0, 0.28, 1)$ (cf. Fig. 2.4), we infer that the magnons in this region have extremely
low group velocity. We correlate this with the lack of change in $q$ which we see in our
data. We propose that due to low group velocity, the information about the disruption
of the magnetic system needs long time to travel across the excited region and create
a new quasi-homogeneous state. Taking into account that the value of $q$ seen in a static
experiment is a net effect of all the interactions between the spins and the lattice, for
the case of relatively weak magnetoelastic coupling, the process of equilibrating the $q$ at
a new value may take more time than the timescale spanned in our experiment.
As the \((0\ q\ 0)\) peak contains contributions from long range order of both \(b\)- and \(c\)-components of magnetization, our results leave open the question whether the melting process happens by the spin system entering directly into the paramagnetic phase, or whether it crosses the sinusoidal phase in between.

### 6.4 Ultrafast melting of anisotropic magnetic correlations and orbital deformations

As discussed in Section 6.2, the \((0\ q\ 0)\) peak investigated with the \(\pi\)-polarized x-ray radiation is sensitive to both \(b\) and \(c\) components of the magnetic structure. Performing a pump–probe experiment probing diffraction peak with a \(\sigma\) polarization would give us sensitivity to exclusively \(c\)-axis correlations. Additionally, looking at the \((0\ 2q\ 0)\) reflection would add the information about the dynamics of the orbital deformation associated with the incommensurate magnetic ordering. Motivated by this, we performed additional experiments at the time-resolved resonant x-ray diffraction endstation at the I06 Beamline at Diamond Light Source (University of Oxford). The measurements were taken by T. Kubacka, L. Rettig, E. Bothschafter, E. Abreu, J. Saari, S. L. Johnson, F. Maccherozzi, Y-W. Liu, S. Dhesi and U. Staub.

#### 6.4.1 Experimental setup

We used the low-alpha mode of the DLS with the time resolution better than 17 ps. Although the pulse duration was almost twice longer than usual due to the cavity fault, it still gives enough time resolution for the expected timescales of \(>20\) ps. The pump laser was operating at 5 kHz repetition rate, with 100 fs long pulses. We estimate the laser spot size to be \(160\ \mu m \times 240\ \mu m\), and the x-ray spot size to be between \(110\ \mu m \times 110\ \mu m\) and \(100\ \mu m \times 140\ \mu m\). The ratio of the spot sizes is a compromise between the pump fluence, average heating and the big enough intensity of diffracted x-ray beam.

The \(b\)-cut \(\rm TbMnO_3\) sample was oriented to put the \(a\)-axis in the scattering plane, in the same geometry as in the previous experiment. It was mounted on the cold finger cryostat, which allowed us to reach nominal temperatures of 12 K. From the temperature dependence of the multiferroic domain contrast we notice a significant offset between the nominal and real \(T_C\) with the pump laser on and off, which we explain as the effect of average heating of the pump laser.

In order to reduce the effect of the average heating, so that the sample still remains in the multiferroic phase, and that its response remains in the regime with the time constant of \(22.3\) ps, we used low fluences for the data collection (\(<1.5\) mJ/cm\(^2\)).
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6.4.2 Results

We measured a series of delay scans with low pump fluences using combinations of incident x-ray polarization, magnetic satellite and laser fluence summarized in Tab. 6.1. We looked at the change of peak intensity, obtaining similar exponential behavior as seen in Fig. 6.3. Additionally, we performed a series of q-scans on the (0 q 0) peak with π-polarized x-rays in longer delay range to investigate the possible q-shift. We precede the description of experimental results and analysis with a short section on validation of the method used for data analysis.

Phenomenological validation of the fitting procedure

To fit the time dependence of the diffraction peak intensity, we use the following model, describing an exponential decay convoluted with the experimental time resolution:

\[ \frac{I(t > t_0)}{I_0} = A(1 - e^{-(t - t_0)/\tau}) \otimes Ne^{-t^2/2\sigma^2} + 1 \]

(6.2)

where the second term is a normalized Gaussian function centered at 0 with \( \sigma = \text{FWHM}/2.3548 \) corresponding to FWHM = 17 ps. Example dataset is shown in Fig. 6.5. In Tab. 6.1 we report the amplitudes \( A \) and time constants \( \tau \) of resulting fit.

We notice that the recorded data is significantly noisier than the dataset discussed in Section 6.3. From the fitting we obtain time constants with values differing from each other by approx. 35%, which possess a relative error of 10–20%, which puts them on the limit of being statistically distinguishable. We also find the decay measured in the (0 q 0)_π channel to have significantly longer time constant than in [154].

Motivated by relatively high uncertainty of \( \tau \), in order to understand the reliability of the fit and improve the precision of fitting, we perform an evaluation of how particular free parameters of the fit influence the uncertainty and values of other parameters (Appendix B). We use a synthetic dataset with parameters chosen to resemble experimentally obtained decay curves. In order to make conclusions about comparability of the timescale seen in two experiments, we additionally analyze how the length of measured delay time range influences the value of \( \tau \) obtained from the fitting. We also estimate the role of the noise level on the decrease of the uncertainties of fit parameters.

We find that both value and uncertainty of \( \tau \) is the most strongly influenced by the letting \( t_0 \) be a fit parameter as compared to freezing it at a particular value. We observe that the fitting algorithm often fails to find a time zero corresponding to its real position, but rather finds the optimal position in the parameter space by compensating for the shift in time zero with the value of delay constant. The values of these two parameters are systematically coupled and when the fit finds \( t_0 \) at earlier delay times than in reality, it follows with finding a larger value of decay time constant. We also learn that although the absolute value of \( \tau \) is influenced by this, when we compare
between two datasets with the shift of $t_0$ between them, the time constants of a particular trace strongly correlate with each other. This means that while the information about the absolute time constant may be uncertain, the difference between time constants measured in two measurements is much less influenced by the shift of absolute position of $t_0$.

Based on this, we perform the analysis in the following way. We first find a position of $t_0$ from the scan made with high pump fluence, where the time constant is significantly shorter and thus gives better sensitivity to $t_0$ position. We then use the obtained $t_0$ as a constant when fitting other datasets, gaining precision of the resulting value of $A$ and $\tau$. To improve the statistical significance, we perform the fits for additional fixed values of $t_0$ and compare the difference between the obtained time constants.

**Time zero estimation**

We estimate the position of time zero from a high-fluence scan with 6.2 mJ/cm$^2$ incident fluence, obtaining $A = -0.943 \pm 0.007$, $t_0 = -2.2 \pm 1.1$ ps and $\tau = 6.6 \pm 1.0$ ps (Fig. 6.6). This is in qualitative agreement with the data collected at LCLS, where almost 100% decay amplitude corresponds to comparably fast time constants. Here however we obtain almost complete melting of the peak for lower fluence, which is below the threshold value for nonlinear response (cf. Fig. 6.3). In agreement with the results from the Appendix B, performing the same fit with $t_0$ fixed at 0 results in shorter time constant ($4.8 \pm 0.6$ ps), however accompanied with significantly worse $\chi^2 = 1.822$, compared to $\chi^2 = 1.267$ when the time zero is taken as a fit parameter. For the analysis of the low-fluence data, we take position of time zero to be $-2$ ps.

Table 6.1: Obtained fit parameters assuming $t_0 = -2$ ps. Values of the uncertainties of the fit parameters (in brackets) correspond to 95% confidence limits. $\chi^2$ is calculated following equation B.1. $R^2$ is the square of the multiple correlation coefficient. $q$ and $2q$ refer to the (0 $q$ 0) and (0 $2q$ 0) diffraction peaks, respectively.

<table>
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<th>$q, \pi, 30K, 0.85mJ/cm^2$</th>
<th>$q, \sigma, 11K, 1.3mJ/cm^2$</th>
<th>$2q, \pi, 11K, 1.4mJ/cm^2$</th>
<th>$2q, \sigma, 11K, 1.4mJ/cm^2$</th>
<th>$2q, \sigma, 11K, 0.5mJ/cm^2$</th>
</tr>
</thead>
<tbody>
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<td>$A$ [$I/I_0$]</td>
<td>$\chi^2$</td>
<td>$R^2$</td>
<td>$T_f$ [K]</td>
<td>$T_f - T_0$ [K]</td>
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<td>0.987</td>
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6.4 Ultrafast melting of anisotropic magnetic correlations and orbital deformations

Figure 6.5: Example of the data with the fit.

Figure 6.6: Estimation of time-zero from the high-fluence scan, \((0 q 0), \pi\text{-polarization, fluence } 6.2 \text{ mJ/cm}^2\)
Decay of intensity of the diffraction peak

We performed a series of measurements on the $(0\ q\ 0)$ and $(0\ 2q\ 0)$ diffraction peaks, for $\sigma$ and $\pi$ polarization of $x$-rays, adjusting the laser fluence if necessary to remain in the regime where the pump does not destroy the peak entirely. In agreement with the experimental data from LCLS, we observe an exponential decay of the intensity of the diffraction peak. Obtained fit parameters and corresponding goodness-of-fit are summarized in Tab. 6.1.

We observe that the $t_0$ position may have shifted between the scans after the realignment of the x-ray beam position and change of the front-end slits settings, and to compensate for this effect, we perform additional fit with the $t_0$ being either a fit parameter, or taking one of the values: $-2$ ps (high-fluence scan), 0 ps (estimated during the experiment), 1 ps (most common result of refinement of $t_0$ by the fit). All fits are characterized with reasonably good $\chi^2$, and the values of $\tau$ obtained for different $t_0$ position differ by 3–7 ps within a given measurement. In the next step, to compare the difference between the measurements taken in different conditions, we look at relative change of $\tau$ as compared with the scan of $(0\ q\ 0)_{\pi}$ at 11 K. The values of $\Delta\tau = \tau - \tau_{q,\pi}$ and $A$ for different scans are schematically compared in Fig. 6.7.

We conclude that, regardless of the time zero position, there are only two main timescales across the data, corresponding to $\sim 35$ ps and $\sim 20$ ps. This trend is accompanied by a similar behavior of the decay amplitude, settling at approx. $-0.45 [I/I_0]$ for the slow-timescale datasets and at approx. $-0.7 [I/I_0]$ and $-0.8 [I/I_0]$ for the faster-timescale datasets.

Following the approach applied in Section 6.3, we estimate the final spin temperature $T_f$ corresponding to the amplitude of the exponential decay $A$ by comparing it to dependence of intensity of diffraction peak on temperature in static conditions (Fig. 6.2). The results are summarized in Fig. 6.7c. Although the pump fluence influences both the dynamic and changes the real base temperature, the temperature rise can be still compared between the scans taken for the same fluence. This is additionally motivated by the relatively linear dependence of the peak intensity on temperature. We estimate the error in the calculation of $T_f$ to be of an order of $\pm 0.5$ K, judging by the uncertainty of $A$ and precision of mapping of $A$ onto the static data from Fig. 6.2.

Based on the three figures in Fig. 6.7, we can conclude the following. The incident 1.55 eV pump pulse with fluence of 1.3–1.4 mJ/cm² corresponds to increase of temperature of 14 K in case of the $(0\ q\ 0)_{\pi}$ peak, which is mostly sensitive to the $b$-axis component of magnetization. The three measurements: $(0\ q\ 0)_{\sigma}$, $(0\ 2q\ 0)_{\sigma}$ and $(0\ 2q\ 0)_{\pi}$ see very similar increase in temperature of 11 K, 20% smaller than $(0\ q\ 0)_{\pi}$. In the same time, the timescale of the dynamics of the same three peaks is very similar, with the time constant shorter than in case of $(0\ q\ 0)_{\pi}$. In agreement with expectations, measurement with lower pump fluence leads to smaller relative increase of temperature.
Figure 6.7: (a) Relative change of $\tau$, (b) corresponding decay amplitude and (c) relative increase of temperature compared for different datasets.
The $(0 \, 2q \, 0)_{\sigma}$ channel experiences longer decay time for lower incident fluences. Additionally, measurements in $(0 \, q \, 0)_{\sigma}$ channel obey the same timescale in either magnetic phase.

**Shift of the peak in $q$**

To investigate the change in $q$, and so to answer the question whether the magnetic subsystem crosses the SDW phase when melting from the MF to paramagnetic state, we measure $\Theta - 2\Theta$ scans as a function of delay for two different fluences (Fig. 6.8).

For low fluence, the peak shifts slightly towards higher $q$, while for higher fluence the change in $q$ is more pronounced and $q$ moves towards smaller values. This behavior is contrary to what one expects from static heating (cf. Fig. 6.1), and looks like apparent “cooling” of the magnetic structure after it is hit by the pump pulse.

This behavior can be explained by taking into account similar pump and probe sizes. For higher fluence we no longer see the contrast between the multiferroic domains, therefore the base temperature of the sample must be above $T_C$ and the crystal is in the SDW phase where the $q$ shows strong temperature dependence. The probe beam sees an inhomogeneous distribution of the pump fluence on the sample (cf. Fig. 6.9 for illustration). High fluence has a double effect on the result of the measurement. First, it rises the base temperature closer to the phase transition or even above $T_C$, lowering the initial peak intensity before time zero. Second, as an ultrafast pump, it makes a bigger fraction of the peak intensity disappear with time. Knowing that high enough fluences will make the diffraction peak disappear to a big extent or even completely, at longer delay times the remnant x-ray diffraction intensity would come mostly from the outer region of the probed area, which felt lower pump fluence. Because this region has a slightly lower base temperature due to the smaller effect of average heating, the $q$ of the diffraction peak would appear as if the sample transited to a state with smaller temperature. We do not see splitting of the peak for longer delays, and it means that the area illuminated by the highest pump fluence disappears without changing the $q$ towards values corresponding to higher temperatures.

**6.4.3 Discussion**

From the comparison of the data from Table 6.1 and Fig. 6.7 and the knowledge about the structure factors coupling to the diffraction intensity at particular $q$, polarization and temperature, we arrive at following conclusions.

We do not see a change of $q$ during the demagnetization observed in the $(0 \, q \, 0)_{\pi}$ channel in $\Theta - 2\Theta$ projection. Contrary, when the peak is pumped away with high enough fluence, it disappears within the same $q$. This points to the scenario that the magnetic system does not equilibrate at a different $q$ within few hundred ps. This can be under-
6.4 Ultrafast melting of anisotropic magnetic correlations and orbital deformations

Figure 6.8: $\Theta - 2\Theta$ scans taken at different fluences. Solid lines are fits to the data using Gaussian function. The vertical dashed line represents the value of $2\Theta$ before time zero. The data is displaced vertically for clarity.

Figure 6.9: Illustration of how the effect of average heating combined with the similar pump and probe spot sizes may lead to the apparent “cooling” behavior of $q$. White regions represent area of the sample covered by high pump fluence, and blue regions represent area of the sample feeling lower pump fluence. The inset illustrates the correspondence between the average heating coming from the pump regions of particular local fluence, and the local base temperature of the sample.
stood by taking into account the low magnon group velocity, and is in agreement with the results obtained in [154].

We see that the intensity in the \((0 \ q \ 0)_{\sigma}\) channel experiences a faster decay with bigger amplitude than in the \((0 \ q \ 0)_{\pi}\) channel. As discussed in Section 6.2, the \((0 \ q \ 0)_{\sigma}\) scattering is sensitive to the \(c\)-axis correlations which only set in at \(T_C\), and arise from the additional noncollinear magnetic order setting in. Meanwhile, the signal in \((0 \ q \ 0)_{\pi}\) contains dominant contribution from the magnetization component along \(b\)-axis which is an easy magnetic axis. This interpretation leads to the conclusion that upon excitation with given pump fluence, the magnetization component along \(c\) experiences smaller change in effective spin temperature than component along \(b\), and nevertheless loses a bigger portion of its long-range order. Therefore the magnetic interactions leading to rise of the \(c\)-axis spin correlations must be generally weaker than the ones causing the \(b\)-axis correlations. This is in agreement with the observation that the SDW-type phases are encountered for higher temperatures than the cycloid phases so they must be strong enough to overcome bigger thermal fluctuations. The bigger stability of the SDW-like spin correlations is in agreement with the observation that the SDW phase is predicted as a typical intermediate magnetic phase within the Landau theory of magnetic crystals [155], while the multiferroic transition replaces the SDW-lock-in transition only for this particular class of compounds because of strong magnetic frustration and staggered Mn–O–Mn bond ordering.

Microscopically, we note that the \(c\)-axis is a hard magnetization axis in the crystal therefore it is not convenient for the spins to be oriented along it unless there is bigger energy cost which needs to be compensated [20]. In case of TbMnO\(_3\), the \((bc)\)-plane is stabilized as an easy plane against the \((ab)\)-plane by additional DM interactions acting across the Mn–O–Mn bond along \(c\) and distorting the AFM alignment (cf. Fig. 3.2). The influence of the pump pulse must relax the additional energy gain coming from the DM interactions and so the spins reorient towards the easy \((ab)\)-plane (cf. Section 3.2.3).

We observe that melting of the spin-spin correlations contributing to the \((0 \ q \ 0)_{\pi}\) in both MF and SDW magnetic phases follows a similar timescale. This supports the idea that the SDW-like correlations are also present below \(T_C\), in agreement with the symmetry arguments that the magnetic order in the MF phase is described by the \(\Gamma_3\) irrep already existing in the SDW phase and \(\Gamma_2\) irrep setting in only below \(T_C\) (Section 2.3.2). Our observation is consistent with the scenario where the SDW phase is prototypical to the cycloid phase and the appearance of the cycloid below \(T_C\) does not involve rearrangement of the spins to a competing phase, but it builds on top of pre-existing correlations.

Turning attention to the behavior of the second harmonic satellites, we see similarity of the signal in channels \((0 \ 2q \ 0)_{\sigma}\), \((0 \ 2q \ 0)_{\pi}\) and \((0 \ q \ 0)_{\sigma}\). We see that these peaks experience both decay with the same timescale and drop in intensity corresponding to
the same increase of temperature. This suggests that they show sensitivity to the same process related to melting of the c-axis correlations. Given that the DM-type distortions cause the incommensurate modification of the orbital order via modulation of the local Mn–O–Mn bond, when the pump pulse reduces their influence causing melting of the non-collinear spin order, it will also destroy the associated orbital modulation. It is supported by the fact that the DM-type distortions distort the Fourier components of magnetic structure away from the single-sinusoidal form, giving rise to higher-order magnetic satellite peaks.

The fact that we observe a fluence-dependent decay-time of the \((0 \ 2q \ 0)\) peak may be explained within a similar picture as the fluence-dependence of the \((0 \ q \ 0)\) peak. As discussed, incommensurate orbital modulation may not come from the spins themselves, but from the oxygen displacements with twice the ordering wavevector. While immediate magnetic disturbance around a photo-implanted AJT polaron is supposed to be contained in the closest vicinity of the excited Mn ion due to the Hund’s energy cost, the strain field around the undistorted site may spread across a longer distance due to the collective character of rotation and distortion of the MnO$_6$ octahedra. This scenario would then predict that the strain-mediated interactions between the excited centers, effectively shortening the decay times, are more significant already for lower fluences than it happens for magnetic-related interactions between AJT polarons. This hypothesis requires nevertheless performing a complete fluence dependence.

Last, we note that the absolute values of the decay time constants do not agree for the \((0 \ q \ 0)\) channel between this experiment and the data related in Section 6.3. One reason for this may be that the repetition rate in this experiment was significantly higher. This leads to different average pump heating, making the base temperature of the sample not uniform and the ground state of the sample before time zero not entirely comparable between the experiments. A more sophisticated explanation involves presence of x-ray assisted processes, happening for intense FEL pulses.

### 6.5 Summary

In this chapter we present a tentative mechanism of how the \(d-d\) transitions contribute to the ultrafast melting of magnetic and orbital order in the spin-cycloid TbMnO$_3$.

The excitation with the 1.55 eV pulses leads to a melting-like process happening to the magnetic structure, which can be described as an increase in spin subsystem temperature. The observed timescales are in qualitative agreement with the values obtained in measurements probing the magnetic contribution to the optical reflectivity, pointing to the spin-spin correlations being destroyed on both short and long-range on a similar timescale.

We observe that during melting, the \(q\) does not move in either \(2\Theta\) or \(\Theta - 2\Theta\) projection. In the static case the value of \(q\) is set by the average GdFeO$_3$ distortion on the one
hand and by the temperature on the other. One could expect that both creation of the AJT polarons and increase of spin temperature could change the value of $q$. Here we explain the lack of transient change of $q$ by low magnon group velocity, hindering the establishment of a new long-range ordering vector on these timescales.

We explain the observation of relatively long demagnetization times for all the peaks investigated within few scenarios, including the sensitivity of the F-type reflections to the additional coupled order parameter, combined effects of spin correlations and lattice distortion preventing the demagnetization by hopping and recombination of the polarons, magnon thermalization time and spin precession timescales.

Among the reasons for which we see different timescales between the $(0 q 0)_\pi$ channel and $(0 q 0)_\sigma$, $(0 2q 0)_\pi$, $(0 2q 0)_\sigma$ channels we point to the sensitivity of the $(0 q 0)_\pi$ peak to a different component of magnetic structure, described by a different symmetry and experiencing stronger stabilizing forces. We propose that the microscopic reason for destabilizing the magnetic component responsible for rise of both cycloidal order and incommensurate orbital order modulation is related to the suppression of energy gain coming from the DM-type distortions acting across the Mn–O–Mn parallel to the $c$-axis. We argue that the SDW-like magnetic correlations are present also in the multiferroic phase. To obtain a less speculative physical understanding, additional modeling would be beneficial to understand what is the relation of the particular multipoles, giving intensity to the investigated diffraction peaks, with their physical counterparts in an incommensurate cycloid system.

It has been proposed that the creation of the AJT polarons play a role in the demagnetization process, as they couple together the electronic, lattice, magnetic and orbital degrees of freedom. In order to gain more insight into the coupling between AJT polarons, magnetism and demagnetization process, one can perform measurements at the diffraction peaks coupling directly to the A-type cycloid, such as magnetic satellite $(0 q 1)$, peaks relating the structural deformations of the Mn–O–Mn bonds or associated with the pure orbital order.

Complexity of the physical processes behind the demagnetization of TbMnO$_3$, and the challenges on the experimental side related to the time-resolved soft x-ray scattering, such as the repetition rate, low diffraction intensities, need for good time resolution and data quality, make this material a good candidate for future experiments at the x-ray FELs.
6.5 Summary
Chapter 7

Ultrafast dynamics of TbMnO$_3$ seen via broadband reflectivity changes

7.1 Introduction

The 1.55 eV pump–resonant x-ray probe experiment tracking the dynamics of the (0 $q$ 0) magnetic diffraction peak has led to a conclusion that the excitation process leads to an incoherent demagnetization on the timescales of more than 20 ps for fluences below 7 mJ/cm$^2$ \cite{154}. The physical process behind the melting of magnetic system was attributed to increase of the spin system temperature due to the excitation with the 1.55 eV. This experiment, however, gave limited insight into the details of the couplings and energy flow pathways.

In the optical regime, narrow wavelength range experiments give only limited information about physical processes leading to change of optical properties at this particular photon energy. Given the complexity of the spectra of manganites in the optical range, tracking the evolution of reflectivity in a broadband range across the range of 2–3 eV would give valuable information about the coupling between the magnetism and optical properties. Additionally, the influence of 1.55 eV pumping on the transient strength of the $d$–$d$ and $p$–$d$ transitions may be related to underlying structural changes.

In LaMnO$_3$, $d$–$d$ excitation led to generation of coherent phonons related to the rotation of the octahedra and straightening of the Mn–O–Mn bonds \cite{8}. While it is expected that similar process will happen in other manganites, probing a broadband reflectivity range would give additional information about coupling of the phonons to the $d$–$d$ and $p$–$d$ electronic transitions via a resonant Raman scattering process.

Additionally, one could expect that the excitation with an optical pulse may lead to a generation of a coherent electromagnon via a stimulated Raman process. Static
7.2 Experimental setup

Raman studies suggest that the visibility of the electromagnon was the biggest around 2.2 eV [106]. Probing large wavelength range would increase the chances of seeing it, due to the enhanced cross-section in detection when approaching an electronic resonance.

In order to investigate further the demagnetization pathway, associated with the long-range melting of magnetic order, and to look into the coherent excitations generated by the pump, an experiment using broadband reflectivity was performed. The wavelength range of the white-light-pulses generated in CaF$_2$ covers well the range of the $d$–$d$ absorption feature present in the optical spectra of TbMnO$_3$. Since it has been shown to respond to short-range spin-spin correlations, tracking the dynamics of the optical response of the sample may give additional insights into the coupling between different subsystems.

7.2 Experimental setup

The experiment was performed using the 1.55 eV pump–broadband reflectivity probe setup in the laboratory of Prof. F. Carbone at Ecole polytechnique fédérale de Lausanne [156]. The measurements were taken by E. Baldini and Dr. A. Mann.

In the setup, the 1.55 eV beam is split and part of it is focused on the sample directly, serving as a pump, while the other part is used for white-light-generation in a CaF$_2$ crystal. Linearly polarized white light beam is focused on the sample using a 10 cm focal-length parabola at an angle close to normal incidence. The reflected beam is collected onto the spectrometer, giving the reflectivity spectrum in 1024 channels uniformly distributed in wavelength range between 406 and 721 nm (corresponding to the photon energies 1.72 to 3.05 eV). The setup was running at 3 kHz repetition rate with the 1.5 kHz repetition rate for data collection determined by the speed of the readout from the detector. To achieve better signal-to-noise ratio the pump beam was chopped using a mechanical chopper. The pump pulse length is estimated at 40–50 fs. The pump beam was hitting the sample surface with the fluence of 5.6 mJ/cm$^2$, where the value of transient reflectivity change both at $t_0$ and at long delays still remains in the linear regime. The polarization the probe was kept parallel to $a$-axis, while the pump was oriented along the $a$-axis for the data with lower time resolution, and either along $a$- or $c$-axis for the data with fine time resolution. The sample was placed in the cold-finger closed-cycle cryostat. For the measurement in the lowest, multiferroic phase, the crystal was kept at a nominal temperature of 8 K as measured by a sensor placed on the cold finger close to the sample. This nominal temperature likely corresponds to a higher real temperature of the sample due to the average heating from the pump.

To obtain a sufficient S/N ratio, for one measurement in every temperature many scans of the delay stage were performed and afterwards integrated to obtain a single pump–probe map. Details of the data preprocessing, including data selection, averaging, group
velocity dispersion effects correction and background subtraction, as well as discussion of data analysis algorithms are described in Appendix C.

Supplementary data to extract the static reflectivity was taken in an ellipsometry experiment in the laboratory of Prof. Ch. Berhnard at University of Fribourg, using a commercial ellipsometer covering the range of 0.5–6.5 eV, equipped with a cryostat. Data were taken by Dr. B. Mallett and M. Yazdi-Rizi. The decomposition of the dielectric function into Lorentzian peaks was performed using program RefFit fitting the real and imaginary parts simultaneously.

7.3 Reflectivity spectra of TbMnO$_3$ in equilibrium conditions

In order to understand the ultrafast response of the reflectivity and disentangle the component of heating of spin system from other factors, a comparison with static values of reflectivity at different temperatures needs to be made. The existing literature data, however, does not provide the dielectric function over a sufficient range of temperatures and suitable polarization of the beam in respect to the crystal axes [94]. To resolve this issue, the dielectric function of TbMnO$_3$ was measured in an ellipsometric measurement at the same temperatures as used in a pump–probe experiment, in the range of 0.5–6.2 eV. The spectra were taken on the same sample and along the $a$-axis, the same as the probe orientation in the time-resolved experiment.

The real and imaginary components of dielectric function of TbMnO$_3$ along $a$-axis are shown in Fig. 7.1a and calculated reflectivity in Fig. 7.1b. Pronounced structure in the range of 2–3 eV is visible, and it appears that in multiferroic phase there are additional fine absorption features visible, either absent or weaker in higher temperatures, however the energy resolution does not allow to refine them exactly in the whole temperature range. The reflectivity of the sample shows behavior corresponding to the increasing spectral weight transfer between the region below 2.5 eV and the region above 2.65 eV, similar to the behavior seen along $b$ axis in LaMnO$_3$ [33, 157]. Between 2.5 and 2.65 eV there is a feature in the reflectivity which seems to qualitatively follow the behavior of the high energy part of the spectrum, however the points at 2.5 eV and 2.65 eV seem to have almost constant reflectivity regardless of the temperature (inset of Fig. 7.1b).

In order to investigate further the spectral structure of the 2–3 eV region, the spectrum at 8 K has been measured with higher energy resolution and the fit involving a sum of lorentzian functions (Eq. 4.6) has been performed using terms suggested by [16]. The results are summarized in Table 7.1 and the corresponding imaginary parts of the dielectric function as well as the fit to the complex $\epsilon$ are illustrated in Fig. 7.2. The model including less parameters gave worse fit in the region of 2–3 eV. The $\epsilon_{\infty}$ was
7.3 Reflectivity spectra of TbMnO$_3$ in equilibrium conditions

Figure 7.1: Dielectric function (a) and reflectivity (b) of TbMnO$_3$ along $a$-axis as a function of temperature.

Figure 7.2: Visualization of the fit and its decomposition into particular lorentzian oscillators

refined at 1.1. The $\chi^2$ of this fit was the smallest from the fits performed with models with different starting points and number of parameters.

One can compare this result with the theoretical spectrum proposed by [16] in Fig. 1.11. The peak at 2.01 eV can be identified with the $d$–$d$ transition feature, however other peaks covered by the range of the pump–probe experiment also have a significant spectral weight. The peaks above 3 eV can be attributed to the $p$–$d$ transitions. In the decomposition we do not see the peaks below 2 eV. Because of significant differences in predicted and observed energies, the attribution of the smaller absorption features
between 2–3 eV to particular transitions with the ones proposed in [16] would not be credible.

A similar spectral-weight-transfer behavior between the $p$–$d$ and $d$–$d$ regions in the parent LaMnO$_3$ has been assigned to the enhancement of the high-spin virtual excitations along the ferromagnetic axis upon lowering temperature [33, 157]. In contrast, in this material the behavior of the fine structure of the 2 eV region is the opposite than in TbMnO$_3$. The spectra of LaMnO$_3$ at low temperature seem to lose the fine structure which may be an effect of being covered by the more strongly enhanced broad feature in the same energy range.

Generally, the position of the main $d$–$d$ feature at 2 eV is in accordance with the literature [16, 31], where it has been suggested that in materials with stronger GdFeO$_3$ distortion the peak center is moved towards higher energies and in the same time the visibility of fine structure is enhanced. The mismatch between expected peak positions and values obtained in this measurement may have different sources, first of them being the alignment of the crystal axes in respect to the beam, as strong anisotropy in the optical spectra is expected [94]. It is also of interest that the goodness of fit in [16] is never evaluated nor compared for particular compounds. Moreover one can expect a big influence on the refinement of the 2–3 eV region coming from the tail of the UV peak not covered by the data, set by [16] in the range of 5.5 eV, while refined here at 9.5 eV. Additionally, their experimental data seem to be in general noisier than the current one, and so their model may need further refinement with data with higher quality.

While it would be interesting to compare high resolution spectra of TbMnO$_3$ with other manganites in order to speculate further on the possible role of the orbital mixing angle [31] and cross-comparison with the Raman experiments, it is beyond the scope of current work.

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7.4 Evolution of the transient reflectivity spectra

The following section describes qualitatively the evolution of the transient reflectivity spectra as a function of delay time and temperature.

First, the behavior of the reflectivity for selected temperatures is described. The four following temperatures have been chosen: 8 K when the sample is the deepest in the multiferroic phase; 30 K when the sample is in the SDW phase; 50 K when the sample has just crossed into the paramagnetic state; 100 K when the crystal is deep in the paramagnetic phase and short-range spin-spin correlations should be negligible. The datasets taken in these temperatures showing the 2D images containing information about dynamics and spectral changes are shown in Fig. 7.3. For the purpose of data analysis, the transient reflectivity spectrum is obtained by integrating a particular region of interest (ROI) of each map within a range of delay times to achieve better S/N ratio. The measurements were taken with time steps of 26.7 fs.

Figure 7.3: Datasets showing full time and spectral change of the reflectivity of TbMnO$_3$ in four different temperatures, corresponding to different types of magnetic ordering. The color scale is adjusted separately for each dataset, however with the position of 0 always corresponding to the same color.
The second part of this section tackles the question if the pump–probe change in reflectivity can be mapped onto the effective temperature, motivated by the behavior of the magnetic correlations seen in the x-ray probe experiment. This is done by comparing the pump–probe spectra with the transformed reflectivity spectra which were taken in an equilibrium experiment as a function of temperature.

### 7.4.1 Time evolution of the transient spectrum

Fig. 7.4 illustrates the spectral dynamics for the sample kept in different magnetic phases. The spectra have been averaged within 134 fs (5 time points) for \( \tau < 1 \) ps and within 670 fs (25 time points) for longer delays.

Right after the pump pulse hits the sample, the spectra taken at all temperatures exhibit the same qualitative behavior. Overall, the reflectivity drops by about \( 1 - 2 \times 10^{-3} \), and this initial drop possesses a distinct spectral structure (dark blue lines in Fig. 7.4). Coming from the low energy side of the spectrum, there is almost no change or slight increase in reflectivity below 1.8 eV. Moving to higher photon energies, the reflectivity change gradually decreases until it reaches minimum around 2.1 eV, the energy close to the middle of the \( d-d \) transition feature. Then the change in reflectivity enters a flat region between 2.2 and 2.5 eV, and around 2.6 eV a peak is visible. Further towards the higher energies, the change reflectivity tends to move back towards zero.

In the delay range of 0.6–1 ps (light blue lines), the change of reflectivity below 2 eV experiences an increase compared to the earlier delay times, while in the higher energy part of the spectrum the reflectivity is constant. The increase in the low-end of the spectrum is so strong that it transiently crosses zero, meaning a transient increase in absolute reflectivity. In 100 K the region experiencing the rise of transient reflectivity extends further in frequency until almost 2.3 eV, so across the \( d-d \) transition peak.

After 1 ps (green and yellow lines) the reflectivity starts to decrease rapidly with the lowest temperatures experiencing the biggest drop, with the exception of the reflectivity spectra at 100 K showing still the same trend but with the amplitude smaller by almost one order of magnitude. Overall, for longer delay times the drop is experienced by the whole spectrum with the magnitude depending on the probe energy. The maximum drop is consistently seen at 2.1 eV, which is close to the middle of the \( d-d \) transition feature. For the data at 8 K with the delay of 12 ps, exhibiting the biggest change, the drop reaches a magnitude of \( 15 \times 10^{-3} \) [dR/R] compared to before time zero, and the slow process happening at long delays accounts for 80% of the total reflectivity change at this photon energy and delay. For the data at 100 K and 12 ps delay the change of reflectivity in the same energy range reaches \( 2.3 \times 10^{-3} \) [dR/R] with the slow process accounting only for 35% of the effect.

In contrast, the height of the peak at 2.6 eV increases with time. This effect is much stronger when the sample is in lower temperature, to the extent that at 8 K
7.4 Evolution of the transient reflectivity spectra

Figure 7.4: Comparison of the time evolution of the spectra in different magnetic phases of the sample. The vertical scale is adjusted separately for each measurement.

Figure 7.5: Differential spectra with the spectrum at 8 K taken as a reference. Inset: a high resolution curve obtained by transforming the reflectivity measured at 50 K and at 8 K (yellow) compared with the scaled and offset transient dR/R at 12 ps and 8 K (gray).
the differential reflectivity crosses zero meaning that transient reflectivity in this region is higher than before time zero. Similar trend can be seen at the very end of the range of the measurement, above 2.8 eV, with the trend suggesting that there is a much higher increase in reflectivity happening towards the UV region.

Moreover, additional fine structure appears in the spectra for the long delay times. This effect is the most pronounced in the 8 K data and almost absent in the 100 K data. Multiple peak-like and wiggle-like structures arise in the region between 2.1 and 2.5 eV, which is the region where many of the weak p-d absorption features were seen in the static data.

### 7.4.2 Comparison with the static data

Taking into account the ultrafast heating of the magnetic structure observed using resonant x-ray diffraction, one can ask a question whether similar effect may be seen in the optical spectrum. In order to answer this question, the static reflectivity is transformed to obtain a differential reflectivity, following the formula

$$\frac{\Delta R}{R} = \frac{R_{\text{pumped}} - R_{\text{unpumped}}}{R_{\text{unpumped}}} = \frac{R_{\text{pumped}}}{R_{\text{unpumped}}} - 1 = \frac{R_T}{R_{8K}} - 1$$

and assuming that the “unpumped” signal is the static reflectivity at 8 K and that the “pumped” signal corresponds to the static reflectivity at a given temperature.

First of all, one can see a remarkable qualitative similarity between such obtained static spectra (Fig. 7.5) and the pump–probe spectra at long delays (Fig. 7.4). Depth of the effect is the strongest around 2 eV and the peak-like feature arises around 2.6 eV. Additionally, the relative reflectivity increase is very pronounced in the region above 2.7 eV, which is on the limit of the energy range of the pump–probe experiment, however agrees with the observed trend. The temperature behavior of the feature at 2.6 eV and the region above 2.7 eV is qualitatively the same.

Additionally, the inset of Fig. 7.5 shows the differential spectrum calculated between the 8 K and 50 K using the data taken with high resolution in photon energy. Remarkably, the fine structure of the reflectivity in the 2–2.5 eV region is also reproduced in a static measurement, more strongly pointing to the scenario where presence of magnetic order is associated with subtle changes to the underlying narrow absorption features. The peak at 2.6 eV does not have the maximum at the same energy as in the pump–probe measurement, however its shape is reproduced almost exactly. With appropriate scaling and shifting in energy by 0.033 eV, the pump–probe spectrum overlaps with the spectrum on Fig. 7.5 in the region of 2.2–2.6 eV, and the biggest drop of reflectivity in both cases happens for the same photon energy, although with different magnitude as compared to the height of the peak at 2.6 eV.

In order to estimate the effective transient temperature by comparison of the pump–probe and static measurements, two effects are taken into account: the height of the peak
7.4 Evolution of the transient reflectivity spectra

at 2.6 eV taken between the maximum of the peak and the baseline corresponding to the values of dR/R right around the peak structure, and the depth of the reflectivity drop at 2.1 eV. In 8 K at 12 ps delay, the height of the 2.6 eV peak is approximately $13 \times 10^{-3} \ [\text{dR/R}]$, which corresponds to the static temperature of 25–30 K and so to the temperature increase of approximately 20 K. The same temperature range is obtained for the depth of the pump–probe effect at 2.1 eV ($15 \times 10^{-3} \ [\text{dR/R}]$). Similar analysis performed for the data at 30 K and 50 K corresponds to a temperature increase of less than 10 K. This discrepancy may be explained by the effect of average heating from the pump laser, which effectively increases the real temperature of the sample, and which is most pronounced at the lowest temperature where the cooling efficiency is the worst. Such an effect is rather unlikely to come from increased pump absorption in this temperature, since there is no jump of the imaginary part of the dielectric constant at the lowest temperatures (Fig. 7.1).

7.4.3 Discussion

The behavior of the transient reflectivity spectra can be tentatively explained as follows.

The structure in the initial drop right after time zero resembles the shape of the inverse of the imaginary part of the dielectric constant (Fig. 7.1). The drop in reflectivity across the whole spectrum seen for early delay times is more pronounced when the sample is at lower temperatures, but its magnitude is comparable for the temperatures with and without magnetic ordering. This would point to the scenario where it is driven by changes in the electronic or structural rather than purely magnetic degree of freedom.

The rise of the reflectivity for delay times between 0.6–1 ps happens at the energy range situated closer to the energy of the pump (1.55 eV, which does not overlap with the center of the broad $d-d$ absorption feature). A delayed response of the reflectivity in the range corresponding to the main part of the $d-d$ absorption peak may be explained assuming that the $d-d$ peak is inhomogeneously broadened, and the energy added to the oscillators with the energies close to the photon energy of the pump needs time to be distributed also to the oscillators with higher resonance frequencies. We note that the region experiencing this transient increase extends to much higher probe energies at 100 K, suggesting that for lower temperatures it may be outweighed by a signal with opposite sign in the range of 2.1–2.3 eV coming for example from the magnetic subsystem.

The process responsible for a drop in reflectivity over longer timescales seems to be much more sensitive to temperature, and qualitatively different behavior at 100 K (no short- nor long-range spin-spin correlations) suggests that this process arises from sensitivity to the magnetic signal. This correlates with the observation that in the static case, there is a significant proportion of spectral weight in this region that has magnetic origin [16, 33, 157].
We observe a fine structure in the spectra in the range of 2.1–2.5 eV, most pronounced at the lowest temperatures. Given the nature of the differential reflectivity measurement, such structures can arise from the changes to these absorption features, such as peak shift, change of peak width or strength or peak splitting or merging. From the transient reflectivity change alone it is extremely difficult to distinguish whether such a structure corresponds to one or more processes happening to the underlying absorption features.

We notice a strong qualitative similarity between the transient spectra and corresponding spectra arising from the static heating of the crystal. By comparing them, we estimate that the effect of the excitation with the pump pulse corresponds to increase of the temperature of the sample on the order of 10–20 K. This is slightly less than the effect seen using the magnetic x-ray diffraction for similar pump fluences and corresponding time delay, but is still roughly on the same order of magnitude (Fig. 6.4). Optical reflectivity and x-ray diffraction are sensitive to different physical phenomena: while the x-rays probe directly the long-range magnetic ordering, the optical reflectivity gives convoluted information via the strength of the electronic transitions, influenced by the spin ordering (probability of the transition depending on the local AFM/FM spin arrangement), lattice and orbital order (GdFeO$_3$ distortion and the effective Mn–O–Mn bond angle and lengths). It is justified to expect that the optical probe is sensitive to a degree of freedom with effectively larger heat capacity and so similar energy flow to the subsystem will result in smaller change of temperature. Additionally, because of the entanglement of various degrees of freedom, the effective temperature change seen in the optical experiment may be an outcome of contributions from the degrees of freedom each having its own temperature.

7.5 Dynamics of reflectivity in a narrowband spectral region

The comparison of the behavior of the transient optical reflectivity spectra with the dynamics of the long-range demagnetization as seen by the x-rays leads to the conclusions that in both cases there are important contributions resembling the equilibrium heating.

In this section, we discuss the comparison of timescales seen in both experiments, paying special attention to the procedures commonly used in order to extract the decay times from the broadband optical reflectivity data. In particular, this dataset turned out to be so specific that none of the simple approaches led to credible results. Having this in consideration, the time dependence is being discussed qualitatively in the next parts of this section. First, the time traces are evaluated at particular regions of interest corresponding to some of the spectral features discussed above. Then, values of transient reflectivity change at a particular delay are evaluated as a function of temperature in order to investigate their sensitivity to the phase transition.
7.5 Dynamics of reflectivity in a narrowband spectral region

7.5.1 Extraction of the time scales

Among most common methods, which are commonly used to extract the decay time constants in broadband reflectivity experiments, are: Single Value Decomposition (SVD), Global Fit Analysis (GFA) and fitting the model function to a single time trace extracted from the broadband reflectivity map (where the time trace is obtained by integration within a large region of interest or an intermediate variable is created, such as transfer of spectral weight).

The Appendix C discusses the challenges which arose when applying the SVD and GFA to extract the time constants from the collected datasets. The data were assumed to arise from a process which could be modeled by a sum of two or three exponential functions. Here a short summary of the analysis is provided.

First, the SVD analysis has been applied to separate the components present in the time traces. However, as exponential functions are not orthogonal to each other, the SVD failed to disentangle them from each other. Instead, the components produced by the SVD are mixtures of the three exponential functions, not preserving their shape and therefore not allowing for extraction of a time constant. Additionally, in presence of noise the cutoff on the distribution of SVD eigenvalues becomes arbitrary and as an effect, some still meaningful portion of data is being entangled with the noise, distorting the spectra and time traces. This is particularly important when looking for longer-wavelength strongly damped coherent oscillations such as electromagnons, since the SVD artifacts can strongly resemble such signals.

GFA typically used for the analysis of time-resolved spectra relies on the assumption that all the spectral regions respond to the same underlying decay process with wavelength-dependent amplitude. In such a complex dataset it turns out that the GFA fails to converge accurately in the whole spectral range, and the number of exponential functions needed is not obvious to determine just by evaluation of the result of the fitting procedure. Possible reasons for this lack of convergence include the presence of a post pulse in the middle of the delay range with the intensity of approximately 5% of the initial pump pulse (see Fig. 7.6 and Appendix C). Additionally, the simple sum of exponentials may not be a good analytical model to describe the observed changes in reflectivity, and it has been shown that the exponentially changing spectral weight transfer does not result in exponentially changing reflectivity [158]; one may need to apply more advanced modeling (stretched exponential, shifted exponential, diffusion models). Moreover, presence of a strain wave—not unlikely given the relatively high pump fluences—with a period comparable with the delay range of the scan would strongly distort the fit convergence. Last but not least, the assumption that there is one common physical process visible across the entire probed spectral range may not be fulfilled.
In a third attempt, the data was integrated within a wide region of interest of 2.14 $\pm$ 0.3 eV (Fig. 7.6), corresponding to the region experiencing the strongest drop of reflectivity and exhibiting the same qualitative behavior, and coupling to the coherent phonons (see next sections). Then the two exponential model function was used to fit the time constants in a delay time range corresponding to $\tau > 0.2$ ps, corresponding to the times after the initial rise has equilibrated. If the underlying decay process is the same within the spectrum, averaging the signal before fitting would be equivalent to averaging the amplitudes of particular exponential terms and so it is a simple way to achieve much better S/N ratio without losing the information on decay processes.

In terms of fit residuals, the double exponential model numerically describes the data well, however it seems that it does not capture the physical process behind the change. First of all, even with the reflectivity integrated in such a wide ROI, the effective delay range of 8 ps (datapoints before the post pulse comes) is not enough when compared with the expected decay times (order of few tens of ps). When evaluating the fit, the algorithm found at least three local minima, depending only on the starting point of the decay time constants with combination with the decay amplitudes. Within such obtained sets of two decay time constants, the shorter time constant would usually vary in the range of 0.7–3 ps, and longer in the range of 5–15 ps, which is shorter than the time constant expected from the x-ray measurement and significantly shorter than the time constants seen in other optical experiments [95, 108] (see Appendix C Fig. C.15 for an example). The dependence of neither time constant on temperature has been reproduced between the sets. Therefore, although the discrepancy between the timescales observed in this and other experiments may have a physical reason, in this particular setting it is more probable that the data do not allow for credible measurement of the real decay time constant out of the used model.

### 7.5.2 Time-resolved change of reflectivity for different spectral regions

In order to analyze the dynamics in time in particular regions of the spectrum, the transient reflectivity vs. delay time is calculated by integrating out the signal spectrally within a particular region of interest. The following ROIs have been chosen: region at the IR end of the accessible probe spectrum (1.73 eV), a region in the middle of the spectrum experiencing the biggest drop in reflectivity (2.09 eV), a region in the flat part of the spectrum (2.40 eV) and finally the height of the peak at 2.59 eV. The transient reflectivity traces as a function of delay time, compared across the temperatures, are visualized in Fig. 7.7. Each set of time traces is supplemented with the values of $dR/R$ at 0.75 ps and at 12 ps, projected onto the $dR/R$ vs. $T$ plane, where the former corresponds to the initial plateau. The available delay range was not enough to cover the full dynamics of transient reflectivity, with exception of the measurements taken at 100 K for the energies above 2 eV, where the reflectivity experiences a step-like decrease.
7.5 Dynamics of reflectivity in a narrowband spectral region

Figure 7.6: Time dependence of reflectivity integrated in a region of interest of 2.14 ± 0.3 eV as a function of sample temperature.

At 1.73 eV, the reflectivity experiences a fast rise right after the initial drop at time zero, which is quickly overtaken by the decay process with a very long time constant, as the curve is almost linearly going down with increasing delay time. The dynamics of reflectivity at this energy is qualitatively different than for the other spectral ranges. It is particularly visible in the 100 K data, where the reflectivity exhibits a finite slope at long delays, in contrast to the step-like behavior for other wavelengths.

The dynamics within regions of 2.09 eV and 2.40 eV is qualitatively very similar. It exhibits a sudden drop in reflectivity at time zero, followed by a plateau region around 0.75 ps. Afterwards the reflectivity experiences a pronounced decay with a shoulder-like shape of the curve.

The dynamics of the height of the peak-like feature at 2.59 eV mirror the dynamics of reflectivity at 2.09 and 2.41 eV. The height of the peak experiences a sudden jump at time zero, then a plateau smoothly transitioning into an increase process with a longer time scale.

7.5.3 Sensitivity to phase transition

Having in mind the discussion regarding limited applicability of exponential fitting in this case, the data are approached using a numerical evaluation of the magnitude of the pump–probe effect at a given delay time. In order to investigate whether the magnitude of the pump–probe effect within these spectral ranges show sensitivity to the phase transition temperatures, the values of dR/R are drawn for the two time points, at 0.75 ps (end of initial plateau—inflection point) and at 12 ps (long time delay). Additionally,
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Figure 7.7: Dynamics of transient reflectivity calculated for different spectral features.
the relative magnitude of the pump–probe effect at 12 ps compared to its value at 0.75 ps is estimated in two ways, by looking at the difference and by looking at the normalized ratio of both. The results are summarized in Fig. 7.8. The open symbols correspond to the vertical axis on the left, and closed symbols to the vertical axis on the right. The data at 1.73 eV are not plotted for evaluation of the ratio because the values at 0.75 ps are too close to zero.

In all cases the magnitude of the effect increases with lowering temperature. The absolute values of reflectivity show the same trend for both delay times. The relative contribution of the long delay time process, calculated by comparing the relative drop between 0.75 ps and 12 ps to the initial plateau at 0.75 ps is significantly stronger at lower temperatures.

The steepest change with temperature is exhibited by the peak at 2.59 eV, with two onset points around roughly 40 K and 20 K (top-right panel in Fig. 7.8). These may correspond to both transition temperatures, assuming that the average heating makes the real temperature of the sample higher than the nominal temperature read off the sensor.
7.5.4 Discussion

We summarize this section with following observations.

First, we find out that the time traces have shapes which cannot be easily fitted using a simple multiexponential function with the timescale identical over the probed spectral range. The datasets exhibit structure which prevents a straightforward application of the standard methods of analysis used for broadband probe experiments. It means that one or more of the assumptions underlying these methods is not met. Such a situation may happen when a relaxation channel becomes activated only after reaching a particular temperature of a subsystem, when different regions within the probed range show sensitivity to different physical processes, or where the energy added by the pump to one degree of freedom flows to other degrees of freedom not simultaneously, but in a sequential fashion. Alternatively, an ordinary exponential function may not be a good enough approximation to describe underlying processes, but more advanced modeling may need to be applied.

Second, from looking at the narrow-wavelength time traces, we see that the region around 1.73 eV exhibits a different slope of the time trace in both high and low temperatures, while the regions in the range between 2–2.4 eV show very similar dynamics, mirrored by the behavior of the peak height at 2.59 eV. We observe a plateau region around 0.75 ps, whose origin may be that the initial short-time-constant recovery process is counterweighed for some time with the second longer decay process arising in the background. Alternatively, such shape of the time trace may suggest that the onset of the decay process, which is dominant at longer delay times, is shifted from time zero towards later delay times. Such behavior could be associated with the presence of degrees of freedom which are not directly coupled to the excitation created by the pump pulse, or that some relaxation pathways are only opened after a threshold energy has been exceeded.

Third, we look at the contribution of the reflectivity drop coming from the long-time-constant process to the overall reflectivity drop as a function of temperature. We notice that all the spectral regions see an increased importance of the long-time-constant processes with decreasing temperature without a clear anomaly at either phase transitions. This is consistent with the results of [16, 108] and points to the scenario where the optical reflectivity is sensitive to the short range spin correlations which are gradually enhanced over wide temperature range.

We see that the feature which is the most sensitive to the magnetic ordering in the pump–probe signal is the height of the peak at 2.59 eV. It most likely corresponds to a modification of the weak features associated with the \( p-d \) transitions at 2.4 eV and 2.65 eV. In \( \text{LaMnO}_3 \) a feature with similar energy of 2.7 eV, unassigned to a particular transition, shows strong renormalization at \( T_N \) [33].
Additional modeling of the feature at 2.59 eV using a phenomenological function, composed of a linearly changing background and the second derivative of a Gaussian function, shows that this it undergoes complex changes both as a function of delay time and temperature (data not shown). Not only the apparent peak amplitude changes, but also its width and position on the photon energy axis. The interpretation of these features is, however, very difficult. One can speculate that because of its high sensitivity to temperature, this peak may be more responsive to the changes of magnetic ordering. However, it is not a feature appearing directly in the dielectric function but in the differential reflectivity and so changes of apparent width or position of the peak in reflectivity cannot be translated directly into an absorption feature changing its width or position. We point out that the static change of reflectivity upon changing the equilibrium temperature also showed a very similar peak shaped feature. Having in mind the comparison between the static and transient reflectivity changes, leading to the conclusion that the main effect of the pump can be described as heating, this peak in reflectivity most likely corresponds to the change of intensity or position of the underlying absorption peaks centered at 2.4 and 2.65 eV corresponding to increasing the temperature. However without careful analysis of the static spectra across many temperatures, the assignment of exact physical mechanism behind this feature in reflectivity has to be left for further investigation.

7.6 Excitation of coherent phonons

Pumping and probing along the $a$-axis of TbMnO$_3$ allows us to see coherent phonons primarily with the $A_g$ symmetry, as it follows from discussion in Section 1.5. From Fig. 3.4 it follows that the electromagnon if excited via a stimulated Raman process could also be visible in this geometry.

In order to investigate whether the excitation of the $d$-$d$ transition with 1.55 eV pump leads to generation of a coherent phonon or electromagnon, a series of measurements with a step size of 13.6 fs has been obtained. At 8 K, two such datasets were obtained: with pump polarized along $a$ and with pump polarized along $c$, in both cases probed along the $a$ axis. Excitation and probing along $a$-axis allows us to potentially see the electromagnon (Fig. 3.4) and $A_g$ phonons. At 30 K, a measurement with pump $a$, probe $a$ configuration was performed. The measurement probing along the $c$ axis did not give reasonable signal to noise ratio due to overall much lower magnitude of the reflectivity change along $c$ axis.

7.6.1 Coherent phonons

The time traces integrated over a wide spectral range show coherent oscillations (for a representative trace measured at 8 K, with the pump $a$, probe $a$ experimental configu-
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Figure 7.9: Coherent phonons in a time trace with high S/N. (a) Reflectivity change as a function of delay time and a fit removing the incoherent background (black); inset: fit residuals. (b) Fit residuals in time domain and frequency domain, where blue curves correspond to the data, and red lines to a fit containing two oscillatory components. (c) FFT of both residuals and their time-domain fit.

The incoherent background is removed by fitting it with the two-exponential function, and the remaining fit residuals are shown in the inset of Fig. 7.9a. The residuals are then fit in the time domain by the model function consisting two damped cosine oscillations, and the FFT of the residuals along with the FFT of the fit is shown in Fig. 7.9b.

The FFT of the residuals (Fig. 7.9b) shows three modes: the dominant one has the frequency of 11.4 THz, and is accompanied by the phonons at 14.7 THz and 15.3 THz (380 cm$^{-1}$, 490 cm$^{-1}$, 510 cm$^{-1}$ respectively). These modes correspond well to the two $A_g(1/3)$ and one $A_g(4)$ modes visible in the static Raman measurement (Fig. 1.10).
The $A_g(4)$ mode is responsible for rotations of the octahedra, while $A_g(1)$ corresponds to the $Q_2$ JT mode, and $A_g(3)$ to the out of phase bending. The highest energy mode has heavily suppressed amplitude, most likely because its frequency is at the limit of experimental resolution. Additionally, the FFT amplitudes have a finite spectral weight around 3–6 THz, however it is rather unlikely that they correspond to a coherent mode due to the lack of clear peak in frequency.

The fit to the residuals in the time domain was performed with a model function containing only two oscillators, as when three phonons were included, the fit result became ill defined due to too many free parameters. It is very likely however that the feature at 15.3 THz corresponds to the real phonon, since its frequency corresponds very well to one of the $A_g(1/3)$ modes, and its amplitude is above the noise level in this frequency range.

The phase of both modes is very similar and equals approximately 1.4 ($80^\circ$). This would point to the scenario that the driving mechanism is not predominantly DECP. Because the pump pulse wavelength is only at the side of the $d$–$d$ transition feature, the expected phase of the phonon is not to be purely cosine like [141]. However, the value of $80^\circ$ phase shift should be taken with much larger uncertainty than the one coming from the fit itself because of possible uncertainty in finding the right position of time zero. For the oscillations with frequency of 11.4 THz, the period of the oscillation is 87 fs. If the assumed time zero position was off by one delay stage step size, the phase change of the oscillation as found by the fit in the time domain would change by approx. $60^\circ$. Therefore it is not unreasonable to estimate the measurement of absolute phase shift to be much less precise and in reality it may be closer to a cosine-like excitation. This reasoning would not affect the observation that both modes have the same phase, pointing to the shared excitation mechanism.

### 7.6.2 Resonant enhancement of phonon detection

The probe spectrum covers many $d$–$d$ and $p$–$d$ absorption features. Therefore one can expect that the amplitudes of the phonons which couple to electronic levels taking part in these transitions will be strongly amplified when the probe wavelength matches the energy of the transition.

In order to see the dependence of the amplitude of phonon oscillation on the probe wavelength, the data was analyzed as following: the data has been integrated within spectral slices with the width of 2 nm across the entire available range. In order to keep fitting artifacts close to minimum, the incoherent background has been subtracted from every slice separately using the following non-physical model function consisting of an exponential function and a third order polynomial with wavelength-dependent fit parameters. The fitting function has been applied only to the data after 0.1 ps delay, in order to remove the influence of the very fast relaxation visible at time zero,
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Figure 7.10: Phonon amplitude as a function of probe photon energy: (a) 8 K, with pump $\parallel a$ and probe $\parallel a$; (b) 8 K, with pump $\parallel c$ and probe $\parallel a$; (c) 30 K, with pump $\parallel a$ and probe $\parallel a$. For comparison, lower panel in (a) depicts the imaginary part of the dielectric constant with the decomposition into absorption features (cf. Fig. 7.2).
7.6 Excitation of coherent phonons

Figure 7.11: The FFT of the residuals integrated over whole range of visibility of the 11.43 THz peak measured in 8 K (a) and 30 K (b) which is likely an artifact coming from the mismatch of the pump and probe pulse lengths. The model function reproduces the incoherent changes very well, however because of the number of terms included, it will fit out all potential low-frequency oscillatory features with the period comparable with the length of the analyzed signal (two inflection points allowed).

By using this procedure, a matrix containing vectors of fit residuals for particular probe energy ROIs is obtained. No phase shift between the oscillations in different spectral regions has been found. The residuals are further averaged within slices of particular energy range on the order of 0.04–0.1 eV, with the exact value chosen separately for every dataset to maintain balance between signal-to-noise ratio of the FFT and the probe-energy resolution of the Raman matrix elements. The fast Fourier transform is then applied to the averaged traces. Thanks to such approach, each spectral bin contains several time traces, and so the approximate error of the measurement can be estimated for every slice.

In order to visualize the sensitivity of the probe beam to the oscillations around 11.4 THz, 14.7 THz and 15.3 THz, the FFT amplitudes are plotted against the middle of the spectral ROI within which the signal has been integrated (Fig. 7.10). In order to account for the non-zero background of the FFT for other frequencies, the plotted quantity is not the Fourier amplitude itself, but its height above the background level. For the symmetric \( A_g \) modes, the oscillation amplitude is related to the Raman matrix elements, which are greatly enhanced when the probe beam wavelength approaches a resonance with the electronic transition in the system.

For data collected at 8 K, the spectral dependence of Raman matrix elements is practically the same regardless the orientation of the pump (Fig. 7.10a–b). The spectra are compared with the decomposed absorption features in the dielectric function (cf. Fig. 7.2). The 11.4 THz peak is visible in a relatively broad wavelength range, between
approximately 1.85 eV and 2.45 eV. This range covers the main \(d-d\) transition feature as well as the \(p-d\) absorption peaks up to 2.45 eV peak. The FFT peak amplitude above the noise level is on the order of \(3 \times 10^{-5} \text{[dR/R]}\). The peaks at 14.7 and 15.3 THz are visible in a narrower region, between 1.85 eV and 2.2 eV, covering the region mostly corresponding only to the \(d-d\) transition feature. Their amplitudes are similar and are of the order of \(1 \times 10^{-5}\) for the 14.7 THz and \(0.5 \times 10^{-5}\) for the 15.3 THz oscillation. The observation that the 11.4 THz phonon and the high frequency phonons resonate in different spectral regions may correspond to real feature, however it can also be an artifact of the data processing. This artifact may be connected with the group velocity correction: modes with higher frequency, which are already at the limit of experimental time resolution, will be much more sensitive to the distortions of the time zero line introduced by imperfect GVD correction, and additionally such imperfection is expected to be more probable at higher photon energies, where the signal is significantly more noisy and the GVD curve more steep.

In the data collected at 30 K, the 11.43 THz peak shows up in essentially the same spectral range as at 8 K, but its amplitude reaches only \(0.6 \times 10^{-5}\). Two higher frequency modes are expected to be analogously lower in amplitude, and within the signal-to-noise ratio it is not possible to confirm whether they are also excited or not.

The FFT of the all fit residuals averaged together for the photon energy below 2.45 eV is shown in Fig. 7.11, confirming the Fourier spectra obtained in Fig. 7.9b. Apart of the modes above 10 THz, in both temperatures there is a finite spectral weight below 5 THz, especially for the 30 K data. However, it is more likely that these features may be an artifact coming from the structured fluctuations of the probe spectrum and intensity, which have not been integrated out perfectly to zero. It is supported by the observation that for test measurements with a different fluence, the \(A_g\) phonon modes persisted, while the region below 5 THz strongly changed.

### 7.6.3 Temperature dependence

Although collected with lower S/N ratio and worse time resolution, the coherent phonon response can be also seen in the long-delay data shown in Fig. 7.6. For each pump–probe map, the spectrum was integrated in the range of 1.85–2.45 eV, which is the whole visibility range of the 11.4 THz phonon. Time traces obtained in such a way were limited to the range of 0.15–4 ps and processed by fitting out the incoherent response and performing the FFT on the fit residuals. The results are shown in Fig. 7.12.

Although the higher frequency phonons are at the limit of resolution of the measurement, the 11.4 THz peak is still visible and persists up to 50 K, so in the paramagnetic phase. The oscillation is absent in the data collected at 8 K which may be explained by a different time resolution of this particular measurement, limiting the visibility of the phonon.
The spectral weight below 3 THz exhibits a structure consisting of spikes with relatively high amplitude. Although it would be tempting to observe a coherent magnon or electromagnon in this frequency range, it is most likely that these are the artifacts coming from non-Gaussian probe spectrum and intensity fluctuations, which creates noise more of a $1/f$ character, where the high frequency components of noise exhibit much less correlated structure than the low frequency components. One can support this conclusion with the observation that there is no consistent temperature dependence of these features, while for the excitation of magnetic modes one would expect strong coupling to the spin correlations and so to the temperature.

### 7.6.4 Discussion

We start the discussion from comparing our results to measurements on $\text{LaMnO}_3$ [8].

First, we observe that upon excitation of $\text{TbMnO}_3$ with the 1.55 eV pump we see essentially the same coherent phonons, connected to the release of the JT distortion via different electronic configuration of the excited Mn ion, and rotations of the $\text{MnO}_6$ oc-
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tahedra activated due to the local change of the magnetic exchange constant leading to shortening and straightening of the Mn–O–Mn bond. Similarly, we observe that the excitation of the $A_g(4)$ mode happens for all the temperatures until 100 K, where our experimental noise level does not allow to resolve the phonon amplitude anymore. Although the 1.55 eV pump is not in resonance with the middle of the $d$–$d$ transition peak, we observe the same modes being excited as in the case of purely resonant excitation with 2 eV photons. This similarity supports the explanation that the $d$–$d$ transitions are the main physical consequence of absorption for the incident 1.55 eV photons.

A significant difference to the measurement on LaMnO$_3$ though is that the $d$–$d$ transition follows with the excitation of three coherent phonons in TbMnO$_3$ instead of two in LaMnO$_3$. We explain this discrepancy by using the observation made in a static non-resonant Raman measurement [26, 29]. In LaMnO$_3$ the $A_g(1)$ and $A_g(3)$ modes are clearly separated in frequency, while in TbMnO$_3$ they are strongly mixed due to the very similar frequencies and the same symmetries (cf. Fig. 1.10). Our measurement supports this scenario. We expect that the absorption of the 1.55 eV photon creates AJT polarons, which locally release the JT distortion, and the accompanying change of the sign of exchange constants leads to Mn–O–Mn bond shortening and straightening [8, 108]. These processes couple the most strongly to the $A_g(4)$ and $A_g(1)$ modes (rotating and JT-stretching of the MnO$_6$ octahedra) via the DECP mechanism: the $d$–$d$ transition couples to the electronic part of the Jahn–Teller effect, which via spin-lattice coupling drives the atoms towards the new equilibrium positions. In TbMnO$_3$ the $A_g(1)$ mode is mixed with $A_g(3)$ mode, so as a result both mixed $A_g(1/3)$ modes couple to the $d$–$d$ excitation.

Interestingly, the modes at 11.4 THz and modes at 14.7 and 15.3 THz may couple resonantly to different electronic transitions. We point out that in case of our experiment, sensitivity via resonant enhancement is in the mechanism of detection and not excitation of particular modes. We are therefore sensitive to the ionic motion modifying particular parts of the bands, and in case when the probe photon energy is in resonance with an electronic transition, the visibility of the modes coupling the strongest to the flat parts of the band structure will be enhanced. We observe that the mixed $A_g(1/3)$ excitation seems to be sensitive mostly to the $d$–$d$ absorption feature, while the $A_g(4)$ mode couples the $d$–$d$ feature as well as $p$–$d$ excitations, with the energies up to 2.45 eV. Since $A_g(1/3)$ contains a strong JT component, it is expected mostly to couple to the electronic transitions across the JT gap, while the $A_g(4)$, involving rotations of the octahedra, may result in changes in the electronic structure involving the Mn 3$d$ as well as O 2$p$ levels. Similar different sensitivity has been seen in a static resonant Raman measurement, where it has been shown that the phonons resonant with the $d$–$d$ transition do not necessarily show sensitivity to a $p$–$d$ transition (cf. Fig. 1.13).

In general, the fact that we see all the phonons in the region responding strongly to the spin correlations is consistent with the GdFeO$_3$ and JT distortions influencing
7.7 Summary

strongly the magnetic order in the crystal. Interestingly, the region between 2.45 and 2.65 eV, where we do not observe higher frequency modes, is also the one which is responding more strongly to the demagnetization at longer time delays. However, one can keep in mind a possibility that the observed difference in mode-amplitude sensitivity to the probe wavelength disappears not due to the physical reasons, but is washed out by the limit of the time resolution of the measurement. Additionally, we note that the phonon enhancement is visible in a different spectral range and leads to a shape of the resonance curve than seen in a static resonant Raman measurement on LaMnO$_3$ [38] (cf. Fig. 1.13c), however in general we should not expect a one-to-one correspondence of the spectral sensitivity between static and ultrafast measurements [141].

Finally, we note that the same phonon modes are activated with the polarization of the pump along $a$ and along $c$ axis, as expected for the $A_g$ symmetry. We do not observe high frequency modes in 30 K, most likely because their amplitudes fall below our sensitivity in dR/R. Additionally, we have not identified oscillations which could be unambiguously assigned to a coherent electromagnon.

7.7 Summary

To sum up the results of the measurements described in this chapter, we state the following.

We have confirmed that the fine structure of the optical spectrum around 2 eV corresponds to multiple $d$-$d$ and $p$-$d$ transitions, however, apart from the dominant $d$-$d$ transition peak at 2.01 eV, the energies of the absorption features do not match well with the values proposed by the theory [16].

After exciting the crystal with pump pulses with energy 1.55 eV, we see rich spectral dynamics. We observe immediate drop in reflectivity, likely coming from the electronic effects. Subsequently we see a plateau lasting of up to approx. 1 ps for photon energies above 2 eV and a transient rise in reflectivity in the IR-end of the spectrum happening meanwhile. On longer timescales we see a drop in reflectivity, the strongest in the region covering the $d$-$d$ and $p$-$d$ features, which we attribute to magnetic signal. The transient reflectivity spectrum in lowest temperatures exhibits a fine structure which may be likely a result of subtle changes to the underlying fine $p$-$d$ absorption peaks.

We notice a strong similarity between the transient spectra and the spectral change associated with static heating. Based on the comparison between the transient and static data, we estimate that the pump pulse causes heating of the sample, quantified by a rise of temperature which is slightly less but comparable with the result seen in x-ray diffraction.

Our signal is not well modeled by a simple sum of exponentially decaying terms, which is likely connected to the IR-end of the spectrum being sensitive to a process with a different timescale, and the dynamics in the region above 2 eV being dominated
Ultrafast dynamics of TbMnO$_3$ seen via broadband reflectivity changes

by the signal coming from spin correlations. It is possible that among many relaxation processes contributing to our data, some of them experience a delayed onset in respect to time zero.

The sensitivity of our signal to the temperature supports the scenario where the optical activity of the features around 2 eV arises from the short range spin correlations. The biggest sensitivity to magnetic signal is exhibited by a feature most likely coming from renormalization of the peak at 2.65 eV, which has been shown to undergo an anomaly at the phase transition in LaMnO$_3$.

In TbMnO$_3$ the 1.55 eV pulse creates three coherent modes which we attribute to the $A_g(4)$ and two mixed $A_g(1/3)$ modes. The detection of the amplitudes of the modes is strongly enhanced for probe energies in resonance with the $d$–$d$ and $p$–$d$ transitions. This suggests that these modes couple strongly to the electronic bands involved in transitions, so mainly $d$-levels of the Mn hybridized with the $p$-levels of the ligand.

We can compare these conclusions with the insight obtained via the x-ray measurements.

In the spectral region responding the strongest to the magnetic signal, we see dynamics following a similar timescale as the demagnetization dynamics seen using resonant x-ray diffraction, confirming that the destruction of magnetic correlations happen on similar timescales in case of long- and short-range order.

Generation of coherent phonons related to the straightening of the Mn–O–Mn bonds points to the conclusion that the crystal in the excited state will on average have smaller amount of bonds which are strongly DM distorted. Following, in the excited state the energy associated with the DM-type interactions will play a smaller role, as they are weaker in case of straighter bonds. This is consistent with the observation made in the x-ray experiment that the magnetic correlations along the c-axis lose a stabilizing interaction arising from the DM distortions.

We proposed that the release of the DM interaction is also responsible for melting of the incommensurate orbital order modulation. As the particular $e_g$ orbital state in an MnO$_6$ octahedron should be associated with certain overlaps between the orbitals of the manganese ion and the orbitals of the ligand, it should also be expressed via the strength of the corresponding electronic $p$–$d$ transition. We speculate that melting of the incommensurate orbital order may be the source of the fine structure appearing in the spectra, which is the most pronounced for measurements taken with the sample in the MF phase. As this additional order appears below $T_C$ and is associated with additional symmetry breaking, it can cause peak splitting or shifting leading eventually to appearance of the structure in differential reflectivity present for both static and transient spectra.

In order to gain further insight into these relaxation processes, more measurements are needed. Particularly interesting would be to measure the transient optical response of the sample above 3 eV, in the region where the trend shows a very strong response.
of the opposite sign than seen for the region around 2 eV. Additionally, checking for presence of phonons with other symmetries (cross-polarization experiment) would give more insight into a degree of undistortion within the AJT polaron. Comparison of the timescales of decay of reflectivity along all three crystal axes could give more information about the preferential relaxation pathways along crystallographic directions with effective FM, AFM and cycloid ordering. One could think of a broadband probe experiment addressing the off-diagonal elements of $\epsilon$, which have been shown to exhibit sensitivity to magnetic phase transitions and can be accessed experimentally by looking at the difference in absorption of the left- and right-circularly polarized light around 2–4 eV [94]. It would be interesting to investigate what is the physical process behind the feature around 1.73 eV. Last, repeated measurement with higher time resolution would help in determining whether the observed resonant enhancement of amplitude of the high frequency phonons is indeed real.
Summary and outlook

The experiments reported in this thesis are a good illustration how technological advances in building new sources of ultrashort electromagnetic pulses and development of new experimental methods enable experimenters to reach to previously inaccessible regimes. Using different time-resolved techniques on a single material, TbMnO$_3$, helped to gain detailed insight into complex couplings between degrees of freedom in this multiferroic crystal and associated timescales.

In the first experiment it was shown that resonant excitation of an IR-active magnetic mode is an efficient way to manipulate the magnetic structure. An intense THz pulse was used to resonantly drive the electromagnon, which arises directly from the coupling between the magnetic and ferroelectric order parameters. Although the theory predicts that the interaction between the electric field of light and spins is mediated by the Mn–O–Mn bond distortion and modulation of the exchange constant, the magnetic structure reacted to the excitation within a fraction of a picosecond. The efficiency of the energy transfer between the laser pulse and the particular mode, characteristic for resonant driving mechanism, resulted in generation of coherent excitation of spins with large amplitude, which suggests a pathway towards ultrafast heatless domain switching in multiferroics.

In contrast, the second experiment proved that after excitation with optical laser pulse, the magnetic order in TbMnO$_3$ undergoes a melting process happening on the timescale of several picoseconds. It was found that the structural destabilization, associated with creation of anti-Jahn–Teller polarons, affects both magnetic order and accompanying incommensurate orbital deformation. The strength of different magnetic interactions, stabilizing long range spin correlations of a particular symmetry across phase transitions, is reflected in melting timescales of corresponding components of magnetic structure.

The third experiment complements the second with the information about the evolution of the spectra in the visible range following the optical excitation. Here the destruction of the long-range magnetic order manifests itself via the strength and renormalization of the electronic $d$–$d$ and $p$–$d$ transitions. The optical excitation is followed with generation of coherent phonons, which proves that excitation of a $d$–$d$ transition in a manganite couples together magnetic, electronic and lattice degrees of freedom.
Overall, the thesis shows that when we manipulate the magnetic structure via the coupled ferroelectric order via resonant excitation of electromagnon, we can achieve macroscopic, coherent changes on the timescale of a fraction of a picosecond. Contrastingly, when we address the magnetic order via the optical $d$-$d$ transition, we achieve incoherent melting of the magnetic correlations on a much longer timescale, which would pose a significant limit on the potential speed of multiferroic switching driven by optical pulses causing spin melting and reorientation. This comparison shows clearly the benefits of using resonant excitation as a means to coherently control the magnetic structure of the sample.

Additionally, in both cases we are able to obtain information complementary to the static measurements. Since resonant x-ray scattering is a direct probe of magnetism, we can directly identify motions of the spins involved in the coherent excitation. Moreover, in an experiment investigating the process of incoherent melting, the time-resolved scattering lets us separate components of magnetic structure following different demagnetization timescales.

As every work, this thesis also leaves some open ends.

A natural continuation of the first experiment is to apply much more intense THz fields to drive the resulting spin motion to nonlinear regime. It should be noted though that TbMnO$_3$ is a good model crystal to gain understanding, but not a good material for applications, mostly due to the low value of $T_C$. Thus a roadmap towards magneto-electric switching should also involve investigation whether this mechanism is a viable route in materials exhibiting multiferroicity at higher temperatures, such as BiFeO$_3$ or hexaferrites, as well as thin film heterostructures.

The experiments involving optical excitation can be continued to answer more fundamental questions about the couplings and interplay of interactions stabilizing the cycloid spin order. In order to separate the influence of Jahn–Teller distortions, one can possibly look at crystals doped with transition metal ions where the same covalence leads to different spin configurations, such as Cr$^{3+}$ or Fe$^{3+}$. Performing time-resolved measurement on the diffraction peaks directly sensitive to the structural and orbital order would greatly contribute to understanding of the couplings in this particular crystal. It would also allow for comparison of the mechanisms observed in TbMnO$_3$ and other single-valent compounds with the dynamics seen in mixed-valence manganites. These and similar fundamental questions are particularly important for strongly correlated systems with such rich physics, and “understanding” is always a first step towards “using”.
Appendix A

Experimental details and data analysis for the THz-pump–x-ray probe experiment

A.1 Experimental details

Experimental setup  The setup is sketched in the Fig. A.1. The experiment was performed at the Soft X-Ray (SXR) beamline at the Linac Coherent Light Source X-ray Free Electron Laser (LCLS FEL) [152], using the Resonant Soft X-ray Scattering endstation [153]. The diffraction peak was measured using the fast-CCD camera (fCCD) [153].

The FEL was operated at a repetition rate of 60 Hz. The x-ray absorption spectrum of TbMnO$_3$ at 15 K was measured around the Mn $L_2$ edge in order to calibrate the incident x-ray energy. The $(0q0)$ peak was measured in the in-plane scattering geometry using $\pi$-polarized x-ray pulses with duration of 100 fs FWHM. Kirkpatrick-Baez optics were used to focus the beam to a spot size with a diameter of 300 $\mu$m.

We used a high power Ti:Sapphire laser synchronized with the FEL trigger to produce 120-fs long pulses with a center wavelength of 800 nm. The main beam was split into three branches: (1) a branch leading to the high-power Optical Parametric Amplifier (OPA), used later to generate the THz pulses, (2) a branch hitting the sample collinearly with the x-rays, used for alignment and timing purposes, and (3) a branch used to determine the mutual time jitter of the x-ray and laser pulses. The x-rays, 800 nm beam and the THz beam entered the sample collinearly.

Overlap and timing  The x-ray penetration depth (0.06 $\mu$m at 652.8 eV) is much smaller than the THz penetration depth (approximately 15 $\mu$m at 1.8 THz in the multiferroic phase [17]). Spatial overlap between the x-ray and 800 nm beams was achieved
A.1 Experimental details

Figure A.1: Sketch of the experimental setup. BS – beam splitter, DS – delay stage, OAP mirror – off-axis parabolic mirror, PD – photodiode, WP – Wollaston prism, IR filter – low-pass filter made from 2 mm thick black polypropylene. For the TbMnO$_3$ measurement, the sample holder was rotated to fulfill the Bragg scattering condition, for the electro-optical sampling and time zero determination the sample holder was rotated to achieve normal incidence of the beam. From [146]. Reprinted with permission from AAAS.

by imaging the x-ray induced fluorescence from a YAG crystal moved to the sample position. The time overlap between the x-ray and THz pulses was obtained in a two-step process using an intermediate overlap with the 800 nm beam. First, we found overlap in time between the x-ray and 800 nm pulses in an x-ray pump, 800 nm probe experiment using 500 µm thick ZnTe crystal placed in the position of the TbMnO$_3$ sample. Soft x-rays excite carriers in ZnTe, inducing a sudden drop in transmittivity of the optical beam, which allows determination of time zero. Afterwards, spatial and temporal overlap between the 800 nm beam and the THz were established using electro-optical sampling on a GaP crystal moved to the sample position. We estimate the accuracy of time zero determination to be 25 fs from uncertainties in the measurement, assuming that the optical response of ZnTe to x-ray excitation is an ideal step function in the limit of zero pulse duration.

The delay time between the x-rays and the THz was changed using a continuously moving encoded mechanical delay stage put in the branch of 1500 nm beam (DL1 on Fig. A.1). For every FEL shot, the jitter between the x-ray pulse and the main 800 nm pulse was monitored using a time-to-space mapping cross-correlator [159], resulting in an effective time resolution of approximately 250 fs FWHM.
THz generation and characterization. The phase-stable, THz pulses were generated using the organic crystal 4-N,N-dimethylamino-4’-N’-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate (DSTMS) \[120\], with a diameter of 6 mm and thickness of 0.59 mm. The DSTMS crystal was pumped with IR pulses with a center wavelength of 1500 nm and a duration of approximately 120 fs FWHM. The THz pulses were polarized horizontally and hit the sample with \( p \)-polarization. Inverting the sign of the THz waveform was achieved by rotating the DSTMS crystal by 180° around the beam propagation direction. The THz beam was focused on the sample using an off-axis parabolic mirror placed inside the RSXS chamber. The THz spot size at focus had a \( 1/e^2 \) diameter of approximately 750 \( \mu \)m.

The shape of the THz waveform was measured using electro-optical sampling \[124\] on the optimally oriented 150 \( \mu \)m thick GaP crystal on 2 mm thick GaP substrate, placed in the position of the TbMnO\(_3\) sample. The maximal modulation of approximately 45% of the electro-optical signal measured with the balanced photodiode corresponds to an amplitude of the electric field of the THz pulse of 300 kV/cm, assuming an electro-optic coefficient of GaP \( r_{41} = 0.88 \) pm/V and refractive indices of GaP \( n_{800nm} = 3.2 \), \( n_{THz} = 3.34 \) \[119, 160\]. Although the absolute sign of the electric field is ambiguous in our measurements, relative changes in the sign of the field on rotating the DSTMS crystal by 180° are well characterized.

Because of the Bragg scattering geometry, the THz beam was incident on the surface of TbMnO\(_3\) at an angle of approximately 63°. The amplitude of the component of the electric field of the THz along the \( a \) axis inside the sample is estimated to be 65 kV/cm, using \( E_{||a} = 1/\sqrt{2} \cdot t_p(\theta_{inc}) \cdot \cos(\theta_{tr}) \cdot E \), where \( t_p = 0.31 \) is the Fresnel transmission coefficient for the \( p \)-polarized field with amplitude \( E \) at the incident angle of \( \theta_{inc} = 63° \), and \( \theta_{tr} \) is the angle between the direction of propagation of the refracted beam and the surface normal. In these calculations we use only the real part of refractive index of TbMnO\(_3\) at 1.8 THz, \( n = 4.31 \), assuming it is equal along \( a \) and \( c \) axes \[17, 85\].

A.2 Data analysis

During the experiment, a large dataset was obtained, which demanded a complex analysis. The following section walks through the main steps undertaken to extract the final experimental results from the raw data. We discuss data processing of the images from fCCD camera containing diffraction peak, calibration of the incident x-ray intensity readout and calculation of the measurement uncertainties.

Calculation of the diffraction intensity. For each shot we extract the intensity of the diffraction peak, the time delay between the pump and the probe and the intensity \( I_0 \) of the incident x-ray beam. The intensity of the diffraction peak is calculated by integration within a set region of interest on the image from the fCCD. For each
A.2 Data analysis

Figure A.2: Example frame from the fCCD integrated for approximately 70,000 shots. Upper panel: raw frame. Middle panel: accompanying background frame. Lower panel: fCCD image after background subtraction.

Figure A.3: Illustration of used regions of interest. Black squares: ROI of the diffraction peak. White square: background ROI.
Experimental details and data analysis for the THz-pump–x-ray probe experiment

Figure A.4: Total number of shots contributing to a time-delay bin for the data shown in Fig. 2A.

shot the image is corrected for the inherent background of the camera by subtracting the background frame recorded before every data run (fig. A.2), and for the short-time-scale drift of the overall readout from the camera by subtracting the intensity integrated within the region of interest placed far away on the detector from the diffraction peak (fig. A.3). The relative incident x-ray pulse intensity is determined for each shot by measuring the photoelectron current from an aluminum-coated foil placed in the beamline [152].

Because the optical delay stage was scanned continuously, the total number of shots contributing to a single data point is different. For data in Fig. 5.2A the total number of shots per data point around time zero is approximately 12 000, while for data in Fig. 5.2B–C it is approximately 5 000. We cut off the delay time at the bin where the number of shots per data point drops to half of the value around time zero (Fig. A.4).

To account for large fluctuations of the x-ray pulse intensity, we use a weighted average to obtain diffraction intensity for one bin for every data run, where we weight the diffraction intensity by the corresponding value of the $I_0$ for all shots. To correct for nonlinearities in $I_0$ readout we use a calibration curve, created by plotting the diffraction intensity as a function of $I_0$ and fitting it with a second order polynomial (Fig. A.5). We assume that the diffraction efficiency of the sample is a function well-described by simply a fraction of incident x-ray intensity and that the readout from the fCCD detector is linear as a function of intensity of the diffraction peak, which is well supported by the fact that the shape of the diffraction peak on the detector barely changes as a function of the x-ray intensity.
A.2 Data analysis

Figure A.5: Data used to calculate the $I_0$ calibration curve.

Figure A.6: Distribution of datapoints within bins corresponding to particular delay times for the pump–probe trace in Fig. 5.2A.
Error bars  In order to calculate the error bars of the pump–probe traces, we split the data runs contributing to a single measurement into slices consisting of approximately 10 000 shots each. For every slice, we extract a pump–probe trace by time-binning the data in 50-fs wide bins. Because the diffraction efficiency of the sample changes with time, we normalize the trace from every slice to the value of the signal before time zero. The traces from separate slices are then averaged to obtain the final pump–probe trace and the error bars for every bin are calculated as a standard error within each bin (bin contents are depicted in Fig. A.6). For data in Fig. 5.2A, B and C the number of slices was approximately 70, 20 and 30 respectively.

The uncertainties for the Fourier-transformed spectra are calculated following [161].
A.2 Data analysis
Appendix B

Fitting of the noisy convoluted exponential signal

It is commonly assumed that, although the mathematical proof holds only in the linear case, in case of non-linear fitting the least-squares-minimization procedure will still give the most likely estimate of the physical value behind the fitted dataset. Here one has to deal with the exponential fit which includes the fit parameters in a nonlinear way, and additionally with the procedure of numerical convolution. In order to get more intuitive understanding of how the convoluted exponential fitting performs in the presence of moderately noisy data, we perform a numerical analysis.

First, we create a model curve, which represents the “real” signal from the sample, with the following parameters: \( t_0 = 0 \) ps, \( A = -0.6 \), \( \tau = 22 \) ps. This curve will serve as a reference to check how well the fitting function performed in obtaining the best estimates of \( t_0 \), \( A \) and \( \tau \). In order to evaluate how the result of the fitting relates to the underlying signal in the presence of noise resembling the experimental conditions, we adapt the following procedure: pseudo-random noise from the Gaussian distribution with the standard deviation close to the experimental value is added onto the model function, and the datapoints are given error bars with lengths corresponding to the experimental conditions (in practice, the two are related with each other).

The analysis is performed as follows. First, in order to see if the model function is the best fit of the data in terms of the least squares, the \( \chi^2 \) value of the model function is calculated, using the noisy dataset as data and an ideal model function as a reference. This value will be compared with the \( \chi^2 \) value obtained after the fitting of the analytical function with parameters refined by the algorithm. This is to evaluate how well the “real data” corresponds to the minimum of \( \chi^2 \) found by the fitting procedure.

Next, the following functions are being fit to the data, where \( A \): amplitude of the decay, \( \tau \): time constant, \( t_0 \): time zero; all functions are multiplied with the Heaviside function starting at \( t_0 \) and afterwards convoluted with a normalized Gaussian function with
B.1 Distribution of \( \chi^2 \) due to added noise

FWHM of 17 ps:

1. \( A(1 - \exp(-(t - t_0)/\tau)) \), with 3 fit parameters: \( A, \tau, t_0 \)
2. \( A(1 - \exp(-(t)/\tau)) \), with 2 fit parameters: \( A, \tau \) \((t_0 = 0)\)
3. \( A(1 - \exp(-(t - 5\text{ps})/\tau)) \), with 2 fit parameters: \( A, \tau \) \((t_0 = 5\text{ps})\)
4. \( A(1 - \exp(-(t + 5\text{ps})/\tau)) \), with 2 fit parameters: \( A, \tau \) \((t_0 = -5\text{ps})\)

The value of 5 ps corresponds to one step of delay stage, and is called here to represent the misplacement of the value of time-zero, hardcoded into the fitting function during the analysis. The fitting is performed for 1000 datasets with the nonlinear-least-squares minimization weighted by the error bars, using a trust-region-reflective algorithm with starting point of \((-0.8, 20, 5)\). The results of the fitting are evaluated in form of correlation plots and histograms to check whether the parameters are interdependent and how the precision of the parameter estimation could be improved.

B.1 Distribution of \( \chi^2 \) due to added noise

First, we estimate how far the noisy data is placed from the underlying “real” model function in terms of the reduced \( \chi^2 \) value:

\[
\chi^2 = \frac{1}{n - m} \sum_i \left( \frac{y_{\text{data}}(i) - y_{\text{model}}(i)}{\sigma_i} \right)^2 \tag{B.1}
\]

The distribution of \( \chi^2 \) for \( 10^4 \) datasets is illustrated in Fig. B.1. It is worth pointing out that because of the addition of noise, for some datasets the model function can correspond to \( \chi^2 > 1.5 \).

Next, the fitting using eq. (1) is performed for the first \( 10^3 \) datasets, minimizing \( \chi^2 \). The comparison of the two distributions is presented in Fig. B.2. It can be seen that consistently across the majority of evaluated noisy datasets, the underlying “real” signal does not correspond to the minimum of \( \chi^2 \), and the fit moves away in the parameter space from the “real” values to converge to the smaller \( \chi^2 \) (visualized as the distribution of the apparent improvement of \( \chi^2 \)). The fitting seems to preserve the width of the overall distribution of \( \chi^2 \) values. The conclusion can be drawn that in the conditions of the real experiment, having only one dataset, it is difficult to argue whether the fit is worse or better if the difference of \( \chi^2 \) values is placed within the range of 0.75–1.25.

Interestingly, when looking at the whole dataset, there is a distinct difference between fits (1),(2) and (3),(4) in terms of apparent improvement of \( \chi^2 \). While the fit functions with correctly placed \( t_0 \) or \( t_0 \) let free as a parameter almost always find a better minimum than the model function, the fits with misplaced \( t_0 \) give \( \chi^2 \) improvement symmetrically centered around 0.
Fitting of the noisy convoluted exponential signal

Figure B.1: Distribution of $\chi^2$, calculated by generating a noisy dataset, and taking the model dataset without the noise as a reference.

Figure B.2: Apparent improvement of $\chi^2$ by fitting. (a) Fit following equation (1) – $\chi^2$ distribution, correlation plot of $\chi^2$ of the model data and $\chi^2$ of the fit, histogram of apparent improvement of $\chi^2$. (b) Apparent improvement of $\chi^2$ achieved by fits with various time-zero values.
B.2 Interplay between time zero and decay time

In the next step, differences between fits obtained using equations (1)–(4) are evaluated. As expected, including additional fit parameter decreases the accuracy of estimation of other parameters (Fig. B.3). Here the error bars are taken as 95% confidence intervals on the fit parameters.

It is interesting to note that it is the time-zero and decay time constant that are most strongly coupled to each other, while the amplitude influences the other parameters less strongly, and is also less sensitive to the presence of another parameter (judging by the correlation coefficients between the vectors of parameters).

For the fit (1), the shift of time zero too much towards the negative delays results in the algorithm finding a longer delay time. This is visible already when looking at the correlation plot between the $\tau$ and $t_0$ (Fig. B.4) and becomes obvious when comparing the correlation plots of $\tau$-s between fits (2)–(4), where moving of time zero results in a shift of decay times. The shift is not only statistical (histograms—Fig. B.5), but also correlated when looking at the correlation plots. It points to the conclusion that accurate estimation of time-zero in a separate experiment may be crucial to obtaining better...
Fitting of the noisy convoluted exponential signal

Figure B.4: Correlation between the estimated $t_0$ and $\tau$ at a local minimum of $\chi^2$

Figure B.5: (a) Correlation between time constants found by fits (2) and (4). (b) Distribution of time constants for the case of different position of time-zero as seen by the fitting function.

accuracy of estimation of a decay time than letting the algorithm adjust the time-zero position as a parameter. Luckily, the shift of time zero seems to affect time constants in a linear fashion, and so while the absolute value coming from the set of measurements may be distorted, they all will be distorted in a similar fashion, making the comparison between them still valid within the error given by the noise in the data (Fig. B.5).

Among the data resulting from fit (1) there were plots were minimum of $\chi^2$ was obtained for almost unphysical sets of values (like $(t_0 \approx -8 \text{ ps}, \tau \approx 35 \text{ ps})$, with perfectly reasonable value of $\chi^2$. While this is in agreement with the statistical character of the measurement, it is a reminder that the good value of $\chi^2$ is never a guarantee of obtaining a “right” result.

Looking at the residuals, it becomes apparent that the most information differentiating between the fits is carried by the datapoints around time-zero. However, here it is almost
B.2 Interplay between time zero and decay time

Figure B.6: Comparison of the three representative noisy datasets with the fit functions resulting in the minimum of $\chi^2$: (a) dataset #505 with the fit recovering well the values of underlying “physical” values; (b), (c) datasets #687 and #967 – two extreme cases corresponding to the time constants much shorter and much longer respectively than the “physical” $\tau$. 

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impossible to differentiate between “good” and “bad” fits by inspecting the residuals. In
Fig. B.6 we plot three datasets, where the noise pattern distorts the result of the fitting
and shifts the refined value of \( \tau \) far away from the underlying “real” value.

### B.3 Influence of cutting the delay time prematurely

A set of data was evaluated where the delay times were cut at 60 ps, in order to check how
big the influence this could have on slightly different values of decay times obtained in
the two experiments. Both datasets were evaluated using fit (2). The histograms of decay
times are shown in Fig. B.7. It is clearly visible that both are centered around the same
value, but overall the fit for the data cut prematurely is much more imprecise. Since in
the experimental conditions only one dataset is drawn out of the whole distribution, it
is much more likely for the data with \( t < 60 \) ps that the fitting parameter will be distant
from the real value. Comparing the fits with the data cut at 60 ps would therefore
most likely lead to more different rather than more similar results between the two
experiments. This is also justified by higher quality of the data taken in the LCLS
experiment.

### B.4 Influence of the length of the error bars

Another dataset with the same noise structure (pseudorandom number generator seeded
in an identical way), but with twice smaller error bars (STD of 0.025) was generated
and analyzed in the same way.

As expected, the errors of the fit parameters decrease accordingly and the fit converges
more clearly around the desired, “real” value. Additionally, the distributions of \( \tau \)-s
coming from fits (1) and (2) become more alike. The systematic change of estimated \( \tau \)
for a particular shift of \( t_0 \) also becomes clearer (Fig. B.8).

The systematic shift in \( \chi^2 \) also changes and now the fits with displaced time zero
converge to significantly worse value (Fig. B.8).
B.4 Influence of the length of the error bars

Figure B.7: Distribution of found decay times in case of fitting to the data in the full and limited \((t < 60 \text{ ps})\) delay range.

Figure B.8: (a): Fitting results for the data with twice as small error bars. (b) \(\chi^2\) improvement for the data with small error bars.
Appendix C

Analysis of the time-resolved broadband reflectivity data

This appendix describes the procedures used to analyze the data, their advantages and drawbacks for this particular dataset. First, a method of discriminating between the good and bad (more noisy, outlying) elements of the dataset is proposed. It was used to process the datasets discussed in Section 7.6. Second, the data preprocessing algorithm is described (background correction, group velocity dispersion (GVD) correction), which was used to process all the pump–probe maps discussed in Chapter 7. Third, methods commonly used to extract information about the dynamics from the pump–probe measurement using broadband optical probe are discussed in terms of their effectiveness on the artificial dataset in the presence of noise. Discussed are the two typically used methods: Singular Value Decomposition (SVD) and Global Fit Analysis (GFA).

C.1 Discrimination of outlying scans

The raw data produced in the pump–probe experiment has a form of two-dimensional matrices with the wavelength along one dimension and the time along the other. For every time point, the pumped and unpumped spectra are collected. Many scans of the delay stage need to be averaged in order to obtain good enough statistics.

There are many sources of noise in this experiment which contribute to the strong non-gaussianity (heteroscedacity) of the noise. One of the strongest being the intrinsic non-reproducibility of the white-light-generation process, which results in strong shot-by-shot changes of probe spectra; additional sources of noise are laser power fluctuations and deposition of matter on the surface of the sample. The main consequence of this fact is that not all the scans may have the same quality and noise distribution. For big enough number of scans, all the noise sources should average out to the Gaussian dis-
C.1 Discrimination of outlying scans

Figure C.1: Correlation between different scans for measurement at 10 K with coarse time resolution. The correlation matrix shows three distinct datasets which are anticorrelated with each other. Additionally, some scans are much more noisy than the rest, and for some scans the magnitude of the pump–probe signal dropped to 60% of the initial value, probably due to the alignment change or change in the sample environment. For final analysis, significant number of scans have been excluded.

Figure C.2: Correlation maps for a long-time delay scan at 11 K. Scan 37 shows significant correlation with the scans 18–26 and 44–50. Further inspection of datafile names shows that they belong to the same dataset and in the experiment were taken in subsequent scans, but were not read in this order into the data-analysis script. The outstanding datasets 27–36 and 28–43 show not only negative correlation of the error structure with the rest of the scans, but also much increased overall noise level and are being discarded from the final averaged map.
Analysis of the time-resolved broadband reflectivity data

Figure C.3: Correlation between different scans for measurement at 10 K with fine time resolution. The scans show much less internal structure. Additionally, high increase in noise and accompanying drop in signal-to-noise ratio is seen for the scans 48–52.

Figure C.4: Correlation between different scans for measurement at 30 K with coarse time resolution. The correlation matrix does not show a strong correlation between the scans which means that they are to much extent statistically independent of each other. Some increase in noise levels can be seen across the scans, however due to similarity of the signal-to-noise ratio and pump–probe signal, only a few scans have been excluded from the final averaging.
C.1 Discrimination of outlying scans

However if we include the scans which are significantly noisier or even not measuring the sample in the same state, these outliers may lead to deterioration of the averaged signal. In order to discriminate the “good” from “bad” scans from a series, a quantitative evaluation scheme based on the error correlation matrices between the scans has been developed.

Analysis of error correlation has been developed in broadband light spectroscopy for molecules [163–166]. Its basic idea explores analysis of correlations between the noise in different channels. The mathematical framework allows for an easy way of modeling and discrimination of various types of noise sources in the experimental data. The noise modeling is far beyond the scope of this thesis, however exactly the same framework can be used to discriminate the good scans from the bad within a dataset. For this, the assumption is made that for the scans taken in similar conditions the noise between the scans will be correlated, while it will be strongly different if the conditions of the measurement changed significantly. Moreover, for the scans suffering from much higher instability of functioning of the laser and higher instability of optical processes like white-light-generation, the overall noise level will be much higher than the other ones.

Numerically, the procedure is as following [164]. Let us take a series of \( r \) scans in form of matrices \( X_k \) (\( k = 1 \ldots r \)), each sized \( (m \times n) \), where \( m \) indicates delay time point and \( n \) – a wavelength in particular channel. \( \bar{X} \) is the average of all scans. The noise needs to be quantified using an estimation of uncertainty of given delay-spectrum point across the whole dataset, and once it is quantified, one can correlate different points and vectors against each other. The measurement error of each scan is estimated according to \( E_k = X_k - \bar{X} \). The information about the measurement error is contained in the rank-3 tensor sized \( (m \times n \times r) \), called the error cube. Symmetrical covariance matrices relating to wavelength-wavelength or time-time error correlations can be built from the error cube by summing out particular dimensions, for example the \( (n \times n) \) spectral correlation matrix is built following the formula:

\[
\Sigma_t = \sum_{k=1}^{r} (x_{k,t} - \bar{x})^T (x_{k,t} - \bar{x})
\]

Here \( x_{k,t} \) is a \( (1 \times n) \) spectrum of a scan \( k \) at a given time \( t \) and \( \Sigma_t \) is a spectral correlation matrix, which is an element \( t \) of the \( (m \times n \times n) \) spectral correlation cube (a rank-3 tensor containing the values reporting correlations between the channels). In an analogous way, an \( (m \times m) \) time correlation matrix evaluated at a wavelength \( l \) can be built using:

\[
\Psi_l = \sum_{k=1}^{r} (x_{k,l} - \bar{x})^T (x_{k,l} - \bar{x})
\]
Analysis of the time-resolved broadband reflectivity data

Here we are interested in looking into correlations between the scans, hence the covariance matrix is built using following relation:

\[
\Xi = \sum_{l=1}^{n} \sum_{t=1}^{m} (x_{t,l} - \bar{x})^T (x_{t,l} - \bar{x})
\]

where \(x_{t,l}\) is the \((1 \times r)\) vector containing the errors of the measurement at particular wavelength \(l\) and time point \(t\), evaluated across the \(r\) scans. For simplicity, the normalization of the matrices by number of elements is not taken into account.

Here the matrices were calculated by taking the differential reflectivity \(\Delta R/R\) at each point as a single measurement \(x\). In order to reduce computational time, the matrices were calculated only in the range limited to half of the delay-time-points, related to longer pump–probe delays. To increase the sensitivity, the part of the spectrum which is inherently much more noisy than the rest has been excluded (224 channels corresponding to the highest wavelengths). Alongside the correlation maps, the pump–probe signal within the same spectral range at the limit of the delay time is calculated, in order to judge the reproducibility of the pump excitation conditions.

Examples of the analysis are given in figs. Fig. C.1–Fig. C.4. Overall, out of the error cube the following quantities are being analyzed in order to discriminate good and bad datafiles:

1. Error covariance matrix and error correlation matrix, which is an error covariance matrix divided by its diagonal \(\Xi_{corr} = \Xi / \sqrt{\text{diag}(\Xi) \text{diag}(\Xi)^T}\), which shows the correlations and anticorrelations among different scans taken in reference to the averaged scan.

2. For every scan, diagonal of \((1 \times m \times m)\) \(\Xi_t\) matrix is calculated, which gives the quantity proportional to the standard error of a point at particular delay time \(t\). In the next step, the standard deviation of the values of this diagonal is calculated. It relates the uniformity of the noise and will be in general greater if the noise (and the data) suffers from bigger fluctuations than the rest of the datasets. Additionally, maximum value of this diagonal is calculated.

3. Diagonal of the error covariance matrix \(\Xi\), where every point is proportional to the generalized standard deviation across all the points analyzed within one scan, including the information from all time points.

4. Depth of the pump–probe effect, integrated across the analyzed spectrum and averaged within the last ten delay time points.

5. Signal-to-noise ratio taken as the ratio of the pump–probe signal and the averaged noise level in a given scan.

These values are being evaluated by hand for every set of measurements. The outlying scans are determined on the basis of the peak values of the noise and mean level of
the noise lying above the average level within the dataset. Additionally, the decrease of signal-to-noise ratio is taken into account, as well as the absolute depth of the pump–probe effect.

In Fig. C.1 the error correlation matrix shows clear distinction between the different measurement series, and the additional difference between the series shows up in the pump–probe signal, which for the last scans is only 60% of the magnitude visible in the first scans. This leads to the conclusion that the datasets should not be integrated together, as they represent different experimental conditions.

Similar effect can be seen in C.2, where it is possible to recover which scans were taken within a single experimental run, but were not read in this order by the data analysis script.

On the contrary, Fig. C.3 shows that most of the scans are uncorrelated with each other, and so there are no big outliers apart from the scans 48–52, which are visibly more noisy than the rest.

Fig. C.4 shows a measurement where almost all the scans were statistically independent of each other, showed similar pump–probe magnitude and signal-to-noise ratio and so most of the maps could have been included in the final averaging.

C.2 Data preprocessing

C.2.1 Averaging scheme

After choosing the “healthy” scans as described in the previous section, the average pump–probe map for measurement at every temperature is created. It has been shown theoretically that in terms of the noise reduction, the best way is to collected differential reflectivity in the balanced detection mode, as otherwise the term relating to noise fluctuations becomes asymmetric in fluctuations and they never average out even with infinite number of scans [164]. Here however such an experimental setting was not possible. We evaluate two methods of calculating the differential reflectivity in this case, namely (1) calculate the differential reflectivity for every scan separately from “pumped” and “unpumped” data, and then average across the scans, and (2) calculate the average “pumped” and “unpumped” data by averaging all the scans, and use them to calculate the change in reflectivity. The latter has been shown theoretically to perform better in case of the numbers approaching zero [167] and this observation is being confirmed in our experimental data. Fig. C.5 demonstrates the comparison of the noise produced by the two averaging schemes described above. First, the average differential reflectivity maps are calculated following the two methods, and then the standard deviation of the signal before time zero is being evaluated separately for every map and wavelength, denoted as $E_1$ and $E_2$ for the method (1) and (2) respectively. The upper figure shows the ratio of $E_1/E_2$ and the lower figure the histogram across the spectrum. It can be
Analysis of the time-resolved broadband reflectivity data

Figure C.5: Representative set of data showing evaluation of the noise resulting from different averaging schemes for a measurement consisting of 35 pre-selected scans of differential reflectivity in the same experimental conditions.

Figure C.6: Raw data file obtained by averaging preselected scans.
C.2 Data preprocessing

Figure C.7: GVD and background correction. The map is multiplied by (-1) for the reasons of the edge-detection algorithm.

Figure C.8: Final map containing GVD and background corrected data, with both wavelength and delay time calibrated in physical units.
seen that the method (2) gives consistently smaller standard deviation than method (1). The improvement is seen especially for the very noisy region in the blue part of the spectrum. Therefore method (2) is chosen for the final data treatment.

C.2.2 GVD and background correction

Differential reflectivity maps need to be treated further prior to the analysis, since they suffer from group-velocity-dispersion effects arising from propagation of broadband beam through dispersive materials, and from a presence of wavelength-dependent background. The correction for the GVD is done using automated edge detection and interpolation. A differential moving average algorithm is used to determine the position of the initial step at time zero for every channel separately. The algorithm is run on a preselected region of data chosen manually in order to increase the reliability of the edge detection. The resulting time zero pixel vs. wavelength channel plots are being subsequently fitted by a 4th order polynomial, and the data are shifted and interpolated so that the dispersion is now zero. In the next step, a region before time zero is averaged in time to get a wavelength-dependent background offset, and the GVD-corrected map is then corrected by subtraction of this offset. The subsequent steps for the representative dataset are illustrated in Fig. C.7–Fig. C.8.

C.3 Methods for data analysis

There are many methods used to analyze such two-dimensional datasets, mainly developed for use in ultrafast absorption spectroscopy of chemical and biological samples [163, 166]. They differ in the extent of the assumptions made about the dynamics of the system, degree of soft and hard modeling, and implementation complexity.

As discussed in the main text, among the most common ways to approach the ultrafast reflectivity data, found in solid state community, are [156, 158]:

1. Singular Value Decomposition of a dataset to reduce the noise and figure out the dominant components
2. Global Fit Analysis, where an assumption is made on the analytical form of the time and spectral dependence of the data and the function is fit to the data using some least-squares method

The applicability of them to the current data analysis is being discussed in the following section.

C.3.1 SVD decomposition

Singular Value Decomposition (also known as Principal Component Analysis) makes an attempt to de-noise the data and determine the eigenvectors of the matrix [166, 168].
It assumes that the matrix can be decomposed in a bilinear fashion into independent orthogonal components. The associated eigenvalues weigh the components in the order of importance. The numerical procedures used are relatively simple and often included in many common programming libraries.

For the data with good signal-to-noise ratio, the SVD can help to determine the number of independent components without prior assumptions regarding the number of elements, which makes it a useful method in soft modeling. It has been shown however, that the presence of noise can significantly reduce the credibility of such a distinction [169]. This effect is evaluated below for a synthetic dataset which was created for the purpose of evaluation of data analysis methods, and then looked at for one measurement of the real dataset.

**Evaluation of the synthetic noisy dataset**

The dataset consists of the set of 6 vectors, containing sum of 3 exponentially decaying functions with different time constants and is visualized in Fig. C.9. The spectral dependence of the amplitudes as well as pure single exponential functions with the unit amplitude is depicted in two lower plots, while the upper plot shows all six vectors.

The SVD decomposition of the dataset produces the eigenvectors visualized in Fig. C.10. While the SVD recovers very well the matrix (residuals on the order of $10^{-14}$), it is immediately clear that neither the spectral dependence of the amplitudes nor the time-dependence of the eigenvectors has been recovered, although the data contained yet no added noise. This is in agreement with the observation that the SVD decomposes the matrix into arbitrary orthogonal functions, and the decaying exponential functions are not orthogonal into each other. When analyzing experimental data, it has also been shown that while the first component follows the physical change of external parameter (e.g. temperature), the second and further components do not [166].

The drastic loss of sensitivity of SVD with added noise is illustrated in Fig. C.11. The synthetic dataset has been multiplied with a Gaussian-distributed noise with predetermined amplitude. The eigenvalues of the decomposition for data with different noise levels show that the SVD drastically loses sensitivity with the noise level, which is depicted by approximately linear dependence on the noise amplitude of the last eigenvalue (upper panel in Fig. C.11). On the other hand, the noise level can be compared with the absolute magnitude of the observed time-dependent change in the lower figure. Noise levels where the SVD still allows for resolution of the third component from the noise are rather unrealistic in a real experiment.

**Evaluation for a real dataset**

The SVD performance is evaluated also for the real data. The data are shown in Fig. C.12, and have been taken with the sample kept in the lowest temperature (below
Analysis of the time-resolved broadband reflectivity data

Figure C.9: Synthetic dataset used to evaluate data analysis methods.

Figure C.10: SVD decomposition of the synthetic dataset without any noise.
C.3 Methods for data analysis

Figure C.11: Illustration of loss of sensitivity of the SVD with increasing level of Gaussian noise in the data. Inset show a magnification of the pump–probe signal to see the relative noise level. The legend refers to the noise amplitude.

The first components are shown in Fig. C.13. The two components carry the most information about the real data evolution. The third component, although noisy, still contains some information at the red-end of the spectrum. The two components are looked upon further in the plots on the right side of Fig. C.13. The first component resembles to much extent a whole pump–probe map. The residuals, composed mostly of the second component, resemble a checkerboard pattern, which may be interpreted as a second orthogonal component with twice the frequency, in an analogy to the Fourier decomposition. The residuals of the first two components resemble a checkerboard
Analysis of the time-resolved broadband reflectivity data

Figure C.12: Dataset used to evaluate the number of exponentials needed for the Global Fit Analysis.

Figure C.13: Evaluation of the components of the SVD decomposition. (a) Decomposition of the test dataset into the first 3 principal components. (b) The first component and its residuals. (c) Sum of the first two components and remaining residuals.
C.3 Methods for data analysis

Figure C.14: Fit residuals after performing the GFA for the case of 2 (a) 3 (b) exponential functions.

pattern with a higher frequency, however they do not form a separate component, as can be seen by comparing them with the residuals of the first three components (upper left panel). The SVD cannot resolve whether the third component is present within the data.

C.3.2 GFA

Global Fit Analysis is a method which demands strong assumptions on the analytic form of the time- and spectral dependence of the data. The equation is then fitted to the whole dataset at once. Very often it is assumed that the process following the excitation consists mostly of simultaneous incoherent relaxation into different channels, which is mathematically expressed as having a sum of independent exponential decays with the amplitudes dependent on spectra and time constants fixed through the dataset:

\[ f(\lambda, t) = C + \sum_{i=1}^{n} A_i(\lambda) \exp(-t/\tau_i) \]

where \( f(t) \) can be in particular a time-dependent differential reflectivity. This assumption is most of the times valid for liquid samples, however realistic modeling of the processes happening in the solid state, involving subsequent energy transfer between different degrees of freedom, may often require significantly more complex modeling approach [170].

The analysis of the SVD decomposition presented in the previous section leads to the conclusion that in the situation when the exact number of exponentials cannot be known in advance from theoretical considerations, it may be very difficult to perform the GFA in a reliable way. One pragmatic approach to solving this problem is to fit
the data with different number of exponential decays and look at the error of the fit parameters. When for $n$ exponentials the fit becomes ill-defined and two time constants seem to converge one into another, it is most likely that the real number of processes is $n - 1$. However, in reality this approach also need to be taken only as a rule of thumb and cases exist when the real number of exponential decays is difficult to disentangle [171]. It is also dangerous when the real time evolution is not described by a sum of exponentials, because contrary to the polynomial functions, the exponentials do not form an orthogonal basis and the fit result may be highly misleading.

Previous research on the optical excitation of multiferroic manganites have shown that at least on a longer timescale of several tens of picoseconds, the dynamics are well represented by the sums of exponentials [95, 108]. However these experiments were not performed with probe wavelength covering the sensitive range of the $d–d$ transition peak. In the following one representative dataset is analyzed using GFA in order to determine validity of fitting the whole map using a sum of exponential functions. Again, the data shown in Fig. C.12 are used for evaluation.

The SVD decomposition of this map has been performed and the plot of the eigenvalues sorted in descending order is presented in the right plot of Fig. C.13. Judging by the values of the eigenvalues, the fit should contain at least two components. For the fitting, the pump–probe map is divided into 2-nm wide slices across the spectrum, and the signal within the slices is averaged in order to obtain better signal-to-noise ratio and limit number of free parameters in the fit. Within the fitting, the time constants are forced to be equal across all the wavelengths, while the amplitudes are allowed to vary freely. No significant difference has been found between different fitting algorithms (trust-region-reflective, Levenberg-Marquardt, robust) and restraining the allowed parameter space has not changed drastically the fit outcome.

The result of the fitting is illustrated in Fig. C.14. The fits were obtained using the function consisting of a sum of two exponential decays (right) or three exponential decays (left), convoluted with the experimental time resolution chosen such that it represents the depth of the initial step. The error bars on the time-constants are approximated by evaluating the hessian of the fit.

For the fit involving three components, the refined time constants were $\tau_1 = 1.45 \pm 0.11$ ps, $\tau_2 = 10.4 \pm 135.2$ ps and $\tau_3 = 10.6 \pm 141.1$ ps. From the values of uncertainties on $\tau_2$ and $\tau_3$ it is immediately visible that the fit is ill defined and following suggestion of [171] one needs to decrease the number of terms involved. For the fit involving two components, we obtained time constants of $\tau_1 = 2.90 \pm 0.25$ ps and $\tau_2 = 5.2 \pm 0.4$ ps. The two-component exponential fit, although started from the initial values very close to ones expected from the 3-exponential fit, did not converge to the same value, and instead stopped at a different set of time constants. The overall goodness of fit judged by the magnitude and distribution of residuals is comparable for both cases. This leads to the conclusion that for the data taken in this time-delay range, signal-to-noise ratio
and with limited insight into microscopic mechanisms driving the relaxation process, it is very challenging to extract reliable time constants straight from the reflectivity data. Such behavior of the fitting may suggest that the multi-exponential model is not a good model for this data in the first place.

**Influence of a post-pulse on the result of the fitting**

In the spectra were integrated within range of 1.85–2.45 eV a kink around 7.97 ps delay can be seen for all the temperatures (Fig. 7.6). This feature can be attributed to a post-pulse. The amplitude of the feature can be read off the residuals of the 2-exponential fit shown in Fig. C.15, and it is approximately 5% of the amplitude of the drop at time zero. Its presence additionally hinders the possible extraction of time constants from the pump–probe traces. The fit results and fit residuals are illustrated in Fig. C.15, and compared for the traces within the whole delay range (left) and the traces cut before the post-pulse sets in (right). It can be seen that the 2-exponential fit describes the short-delay data reasonably well, while for the fit performed on the whole trace, the fit residuals show strong mismatch between the shapes of the model curve and
the experimental data. Moreover, the fitted time constants differ significantly between both cases, however this is influenced as well by a much shorter delay range.

C.3.3 Outlook

There are many other algorithms designed in order to efficiently and reliably extract information from such data. Their disadvantage is, however, that they are not as easily implementable as the SVD and GFA. Unluckily, solutions developed and made public by other research groups do not give any further insight into the data, or at the time of writing this text, have not functional (Ultrafast toolbox 1.0, OPTIMUS toolbox 2.08, MCR-ALS 2.0).

Among other algorithms, it would be advisable to look at the Independent Component Analysis instead of the SVD. It has been shown to successfully decompose noisy data into physically meaningful vectors and has been shown to perform well in the domain of spectroscopy [166].

Instead of trying to evaluate the time constants by means of GFA with predefined number of components, another approach may be used to directly calculate the lifetime of the process. Such procedures have been developed for purpose of fluorescence, NMR and other spectroscopic methods dealing with exponential decays. Among them one can reach into methods giving the lifetime spectrum of the time-dependent data, based on Laplace transform, or some more sophisticated decomposition algorithms.

More physically meaningful insight may be still taken using GFA or SVD, but not on the differential reflectivity data directly. It has been shown that the physical quantity, following the exponential decay, may not be reflectivity itself, but rather a spectral weight transfer [158] or the amplitude of the absorption feature [156]. Here the difficulty may lie in a fact that the time-dependent behavior of the blue-end of the spectra point to additional, very strong process happening in the region of the UV, beyond the resolution of the spectrometer. This may prove the spectral resolution very difficult and the Kramers–Kronig approximation impossible to use in a straightforward fashion.
C.3 Methods for data analysis
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*Temperature-dependent electron-phonon coupling in La$_{2-x}$Sr$_x$CuO$_4$ probed by femtosecond x-ray diffraction*

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**Conference contributions**

**Oral presentations**

*Dynamika spinów w multiferroiku wywołana ultrakrótkimi impulsami promieniowania terahercowego* (in Polish, invited)

XLIII Zjazd Fizyków Polskich (XLIII Meeting of Polish Physical Society), 6–11.09.2015, Kielce, Poland

*Large amplitude spin dynamics driven by a THz pulse in resonance with an electromagnon* (invited)

12th International School and Symposium on Synchrotron Radiation in Natural Science, 15–20.06.2014, Warsaw, Poland

*Direct view of spin dynamics in a large magnitude coherent electromagnon*

ELI-ALPS 1st User Workshop, 21–22.11.2013, Szeged, Hungary
Selected poster presentations

*Ultrafast dynamics of TbMnO$_3$ seen via broadband reflectivity changes*

*Large-Amplitude Spin Dynamics Driven by a THz Pulse in Resonance with an Electromagnon*
(the poster won a Best Poster Award)
Science @FELs 2014, 15–17.09.2014, PSI, Villigen, Switzerland

*Ultrafast dynamics of optically pumped spin-cycloid multiferroic*
PIPT5 (Photoinduced Phase Transitions and Cooperative Phenomena), 8–13.06.2014, Bled, Slovenia

*Direct view of spin dynamics in a large magnitude coherent electromagnon*
Dynamic Pathways in Multidimensional Landscapes, 16–20.09.2013, Berlin, Germany

*Towards femtosecond dynamics in multiferroics*
505. WE-Heraeus-Seminar on New Routes to Single-Phase Multiferroics, 23–25.04.2012, Physikzentrum Bad Honnef, Germany

*Towards femtosecond dynamics in multiferroics*
5th European School on Multiferroics, 29.01–3.02.2012, Monte Verita, Switzerland
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