Ph.D. thesis

Optical study of spin excitations in multiferroic crystals

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Motivation

In the course of geometrical optics, one of the main principles is Helmholtz’s reciprocity theorem [1–3] stating that counter-propagating light rays follow the same path and experience the same refractive index. However, recent optical studies on low symmetry systems indicate the violation of this principle. Specifically, some materials are able to distinguish between counter-propagating light beams, as the beams propagating opposite to each other experience different refractive indices and absorption coefficients. [4, 5] In most of the systems the difference is rather small, barely reaching 0.1% in the studied quantity.

In contrast, in magnetoelectric multiferroic materials, which show simultaneous ferroelectric and magnetic ordering, the absorption coefficient can drastically differ for counter-propagating light beams [6, 7]. These materials offer the possibility of their future applications as optical diodes transmitting light in one but not in the opposite direction. However, the spontaneous electric and magnetic order in most multiferroic crystals known up to now only exist at cryogenic temperatures, seriously limiting the practical applications. Clarifying the fundamentals of the non-reciprocal optical phenomena and its enhancement in multiferroic crystals will help in designing and discovering novel materials that work at room temperature and beyond, opening the road to applications.

The aim of my Ph.D. research was to contribute to a better understanding of this fascinating phenomenon and to the solution of the problems prohibiting its applications.
Chapter 1

Introduction

1.1 Magnetoelectric coupling in multiferroic crystals

Originally the term magnetoelectric multiferroic referred to compounds with ferromagnetic and ferroelectric orders coexisting in a single phase. Nowadays, this terminology is used in a broader sense, when ferroelectricity is accompanied with long-range magnetic orders, including ferromagnetism, ferrimagnetism and even antiferromagnetism. If the magnetic and the ferroelectric orders are not just coexisting but also entangled with each other, the material is expected to show strong magnetoelectric (ME) effects. In a phenomenological description, in analogy with conventional magnetic and electric susceptibilities, the $\chi_{\alpha\beta}^{\text{me}}$ magnetoelectric susceptibility tensor can be introduced by adding a $F^{\text{me}} = -\chi_{\alpha\beta}^{\text{me}} H_\alpha E_\beta/c$ term to the free energy density. Here $\alpha$ and $\beta$ stand for the Cartesian coordinates, $c$ denotes the speed of light in vacuum, and $E_\beta$ and $H_\alpha$ are the components of the electric and magnetic fields, respectively. Due to this cross coupling, external electric and magnetic fields can also induce magnetization and polarization response, respectively,

$$\Delta M_\alpha = \frac{\varepsilon_0}{\mu_0} \chi_{\alpha\beta}^{\text{me}} E_\beta \quad \text{and} \quad \Delta P_\beta = \frac{1}{c} \chi_{\beta\alpha}^{\text{em}} H_\alpha. \quad (1.1)$$

Here $\varepsilon_0$ and $\mu_0$ are the vacuum permittivity and permeability, respectively. The two cross-coupling tensors are connected by the $\{\ldots\}'$ time-reversal operation according to $\{\chi_{\alpha\beta}^{\text{me}}(\omega)\}' = -\chi_{\beta\alpha}^{\text{em}}(\omega)$, where $\omega$ is the angular frequency. In the static, $\omega = 0$ case the magnetoelectric susceptibility has to be odd with respect to the time reversal, since $M$ and $H$ are odd, while $P$ and $E$ are even. Thus in the static limit $\chi_{\alpha\beta}^{\text{me}} = \chi_{\beta\alpha}^{\text{em}}$, i.e. the two tensors are the transposed pairs of each other.
According to Neumann’s principle [8], besides the general relation above, the magnetoelectric tensors should also reflect the ground-state symmetry of the magnetic crystal. When considering the uniform, i.e. long-wavelength response of the system, the elements of the magnetic point group provide the constraints on the tensor elements. In general, magnetoelectric susceptibility is finite only in materials breaking the spatial inversion symmetry, since it connects quantities with different spatial parity (\(M\) and \(H\) are preserved, while \(P\) and \(E\) are reversed upon inversion symmetry). The result of such an analysis on the static magnetoelectric susceptibility can be found for all magnetic point groups in Ref. [9].

Beyond the phenomenological description, it is possible to treat the magnetoelectric effects on the microscopic level by describing the relation between the local electric polarization and the spins. Indeed, revealing and understanding different mechanisms of the spin-driven or spin-induced ferroelectric polarization is the most fundamental issue in the research of multiferroic materials. Although the spin \(S\) is a time reversal odd vector operator with axial vector character and the electric polarization \(P\) is a time reversal even polar vector, quadratic or bilinear expressions of spin operators have the same transformation properties as the components of the electric polarization vector, i.e. they can belong to the same irreducible representation of the magnetic point group of the crystal. [10] Therefore, such bilinear or quadratic expressions of spin operators have a linear relationship with the electric polarization.

Magnetoelectric coupling can originate from a single magnetic site, whose spin-driven site polarization is described by quadratic expressions of its single spin, or from a bond between two magnetic sites, where the spin-induced bond polarization is described by bilinear expressions of the components of the two spin operators. Based on the more throughout study in Ref. [10] I briefly discuss the symmetry aspects of these single-site and single-bond magnetoelectric mechanisms.

The single-site magnetoelectric coupling is only possible in non-centrosymmetric crystals, since the electric polarization is odd, while any combination of the spin operators of a single ion is even with respect to the spatial inversion, thus in the presence of inversion symmetry they cannot be equivalent. Since symmetrized second order spin expressions are only non-trivial, i.e. not equivalent to linear expressions of the spin components, for \(S \geq 1\), single-site magnetoelectric coupling can appear only in \(S \geq 1\) spin systems. Bilinear or quadratic expressions of the components of a single spin are also proportional to the corresponding bilinear or quadratic form of the polar vector components \(r_i^\alpha\), since the differences in the geometrical transformation properties of the polar and axial vector components under mirror plane reflections

\[5\]
and inversion cancel out in the symmetrized bilinear/quadratic expressions: \( r_i^\alpha r_i^\beta \sim (S_i^\alpha S_i^\beta + S_i^\beta S_i^\alpha)/2 \). Thus, one can easily assign all possible bilinear or quadratic spin terms which can be associated with electric polarization using the character table of the point group of the local symmetry around the magnetic site: the linear terms and bilinear/quadratic expressions of polar vector components belonging to the same irreducible representation correspond to the components of the electric polarization and their representations in the spin space, respectively. The microscopic mechanism behind the single-site electric polarization is the spin-dependent metal-ligand hybridization [11]. In case of a magnetic ion surrounded by an inversion-breaking tetrahedral oxygen environment it can be expressed as

\[
P \sim \sum_{i=1}^{4} (S e_i)^2 e_i,
\]

where \( e_i \) is the unit vector pointing from the metal ion to the \( i \)th ligand. [12]

The details of the quantum-mechanical derivation of Eq. 1.2 can be found in Ref. [10]. In Chapter 4 I will discuss the emergent static and dynamic magnetoelectric properties of materials hosting the single-site magnetoelectric coupling.

In contrast to the single-site case, single-bond polarization can also emerge in centrosymmetric materials, since the inversion exchanges the two metal ions, thus reverts the role of the two spins. This means that in centrosymmetric materials only antisymmetric combinations of the two spins can carry electric polarization. On the other hand, when indexing the spin sites in the opposite way, the observed polarization cannot change, thus the expression of the polarization has to contain the \( e_{12} \) unit vector pointing from the site of \( S_1 \) to the site belonging to \( S_2 \). Thus, in centrosymmetric materials the general form of the single bond polarization for a bond connecting magnetic moments of the same lengths reads [13]

\[
P_{12} = P^{sc} e_{12} \times (S_1 \times S_2) + P^{ml} ((e_{12} S_1) S_1 - (e_{12} S_2) S_2),
\]

where \( P^{sc} \) and \( P^{ml} \) are the coupling constants corresponding to the spin-current and metal-ligand hybridization mechanisms, both of them originating from the spin-orbit coupling. In the first case non-parallel magnetic moments result in a spontaneous spin current. [14] Indeed, the spin current has the same spatial and time-reversal transformation properties as the time-reversal even polar vector of the electric polarization. This mechanism is also referred to the inverse Dzyaloshinskii-Moriya mechanism, since a non-collinear alignment of the spins changes the bond angle, whereas the direct Dzyaloshinskii-Moriya effect accounts for non-collinear spin orders due to the
deviation of the bond angle from 180°. Note that the second term due to metal-ligand hybridization is the difference of the single-site polarizations of the two magnetic ions, since the ±\( \mathbf{e}_{12}/2 \) vectors pointing from metal ions to the ligand have opposite signs.

Besides the above mentioned mechanisms, in non-centrosymmetric materials a symmetric expression of the two spins can also result in electric polarization. The exchange energy gain of the two spins depends on the length and the angle of the connecting metal-ligand-metal bond, thus, under the right circumstances the collinear spin order can produce an electric polarization. This magneto-striction mechanism can be described as \( \mathbf{P}_{12} = P^{\text{ms}} \mathbf{e}_{12} (\mathbf{S}_1\mathbf{S}_2) \). Since this mechanism does not involve the relativistic spin-orbit coupling, the magnitude of the corresponding polarization can be larger as compared to the single-site and spin-current polarizations. [15]

### 1.2 Dynamic magnetoelectric effect

The microscopic description of the linear response of a quantum system to external stimuli is given by the Kubo formula. [16] For the frequency dependence of the electric, magnetic and magnetoelectric susceptibility tensor, the finite-temperature Kubo formula reads as

\[
\chi^{ee}_{\gamma\delta}(z) = -\frac{V_c}{\varepsilon_0 \hbar} \sum_{m,n} \frac{e^{-\beta \hbar \omega_m} - e^{-\beta \hbar \omega_n}}{\sum_i e^{-\beta \hbar \omega_i}} \frac{\langle n | P_\gamma | m \rangle \langle m | P_\delta | n \rangle}{z - \omega_m + \omega_n},
\]

\[
\chi^{mm}_{\gamma\delta}(z) = -\frac{\mu_0 V_c}{\hbar} \sum_{m,n} \frac{e^{-\beta \hbar \omega_m} - e^{-\beta \hbar \omega_n}}{\sum_i e^{-\beta \hbar \omega_i}} \frac{\langle n | M_\gamma | m \rangle \langle m | M_\delta | n \rangle}{z - \omega_m + \omega_n},
\]

\[
\chi^{me}_{\gamma\delta}(z) = -\frac{V_c}{\hbar} \sqrt{\frac{\mu_0}{\varepsilon_0}} \sum_{m,n} \frac{e^{-\beta \hbar \omega_m} - e^{-\beta \hbar \omega_n}}{\sum_i e^{-\beta \hbar \omega_i}} \frac{\langle n | M_\gamma | m \rangle \langle m | P_\delta | n \rangle}{z - \omega_m + \omega_n},
\]

respectively, where \( z = \omega + i\varepsilon \) and \( \varepsilon \to 0^+ \). \( M_\gamma \) and \( P_\delta \) are the operators of the magnetic and electric dipole density, respectively. \( |m\rangle \) and \( |n\rangle \) are eigenstates of the unperturbed system with energies of \( \hbar \omega_m \) and \( \hbar \omega_n \), while \( \beta = (k_B T)^{-1} \) is the inverse temperature and \( V_c \) stands for the volume of the unit cell. In the zero-temperature limit the Boltzmann factors vanish except for the \( |0\rangle \) zero energy ground state. Using the limit \( \lim_{\varepsilon \to 0} \frac{1}{\varepsilon + i\varepsilon} = \mathcal{P} \frac{1}{x} - i\pi \delta(x) \) identity, the real
and imaginary parts of $\chi^{me}_{\gamma\delta}(\omega)$ can be separated according to

$$
\Re \chi^{me}_{\gamma\delta}(\omega) = -\frac{V_c}{\hbar} \sqrt{\frac{\mu_0}{\varepsilon_0}} \sum_{m} \left[ \mathcal{P} \frac{2\omega_m \Re \langle 0 | M_\gamma | m \rangle \langle m | P_\delta | 0 \rangle}{\omega^2 - \omega_m^2} \right] + \pi \sum \langle 0 | M_\gamma | m \rangle \langle m | P_\delta | 0 \rangle \delta(\omega - \omega_m) - \delta(\omega + \omega_m)), \tag{1.7}
$$

$$
\Im \chi^{me}_{\gamma\delta}(\omega) = -\frac{V_c}{\hbar} \sqrt{\frac{\mu_0}{\varepsilon_0}} \sum_{m} \left[ \mathcal{P} \frac{2\omega_m \Im \langle 0 | M_\gamma | m \rangle \langle m | P_\delta | 0 \rangle}{\omega^2 - \omega_m^2} \right] - \pi \Re \langle 0 | M_\gamma | m \rangle \langle m | P_\delta | 0 \rangle \delta(\omega - \omega_m) - \delta(\omega + \omega_m)) \tag{1.8}
$$

These expressions can also be obtained by second order perturbation theory. [17] The real/imaginary part of the $\langle 0 | M_\gamma | m \rangle \langle m | P_\delta | 0 \rangle$ transition matrix element product is antisymmetric/symmetric under time reversal, respectively, since time reversal changes sign of the magnetic dipole operator and also requires the conjugation of the matrix elements due to the exchange of the initial and final states. From the Kubo formula it is also easy to show that time reversal connects the two magnetoelectric tensors according to $\chi^{me}_{\gamma\delta}(\omega)' = -\chi^{me*}_{\delta\gamma}(\omega)$. Considering the zero-frequency limit in Eq. 1.7, due to the Dirac delta function, the imaginary part of the matrix element product disappears in the real part of the magnetoelectric susceptibility.

To study the light propagation in magnetoelectric media, one needs to include the $\hat{\chi}^{me}$ tensor in the material equations when solving the Maxwell equations. Due to the low symmetry of ME materials, the dielectric permittivity ($\hat{\varepsilon}$), the magnetic permeability ($\hat{\mu}$) and the ME susceptibility tensors have complicated forms, the quartic equation for the index of refraction is usually difficult to solve analytically. However, since the diagonal components in the $\hat{\varepsilon}$ and $\hat{\mu}$ tensors dominate over their off-diagonal components, in the leading order the index of refraction is given as

$$
N^\pm(\omega) \approx \sqrt{\varepsilon_{\delta\delta}(\omega)\mu_{\gamma\gamma}(\omega) \pm \frac{1}{2} \left[ \chi^{me}_{\gamma\delta}(\omega) - \chi^{me*}_{\delta\gamma}(\omega) \right]}, \tag{1.9}
$$

Here $N^\pm$ stands for the refractive indices of waves propagating in opposite directions ($\pm \mathbf{k}$). The $\delta$ and $\gamma$ coordinate axes are parallel to the direction of the electric ($\mathbf{E}^\omega$) and magnetic ($\mathbf{H}^\omega$) fields of light, respectively.

By applying an external static magnetic field one can change the magnetic ground state of the system, and together with the ground state $\hat{\chi}^{me}(\omega)$ is changed as well. In fact, $\hat{\chi}^{me}(\omega)$ also changes when the field only alters some of the excited states but not the ground state. Thus, it is reasonable to consider the

$$
\chi^{me}_{\gamma\delta}(\mathbf{H}, \omega) = \sqrt{\frac{\mu_0 \mathcal{P} M_\gamma(\mathbf{H}, \omega)}{\varepsilon_0 \partial E_\delta(\omega)}} \tag{1.10}
$$
differential ME susceptibility when describing optical processes in $H$, external magnetic field. In the following I will always use the differential definition of the susceptibility and omit the magnetic field argument.

The dynamic magnetoelectric effect can break the reciprocity in optical processes. This can be easily seen by considering the oscillating polarization and magnetization induced by the light beams counter-propagating with each other. For $+k$ propagation direction

\[ P_\delta^{\omega} = \chi^{ee}_{\delta\delta}(\omega)E_\delta^{\omega} + \frac{1}{c} \chi^{em}_{\delta\gamma}(\omega)H_\gamma^{\omega} \]  
and

\[ M_\gamma^{\omega} = \chi^{mm}_{\gamma\gamma}(\omega)H_\gamma^{\omega} + \sqrt{\frac{\varepsilon_0}{\mu_0}} \chi^{me}_{\gamma\delta}(\omega)E_\delta^{\omega}, \]

while for the $-k$ direction the relative signs of $E_\delta^{\omega}$ and $H_\gamma^{\omega}$ is opposite,

\[ P_\delta^{\omega} = \chi^{ee}_{\delta\delta}(\omega)E_\delta^{\omega} - \frac{1}{c} \chi^{em}_{\delta\gamma}(\omega)H_\gamma^{\omega} \]  
and

\[ M_\gamma^{\omega} = -\chi^{mm}_{\gamma\gamma}(\omega)H_\gamma^{\omega} + \sqrt{\frac{\varepsilon_0}{\mu_0}} \chi^{me}_{\gamma\delta}(\omega)E_\delta^{\omega}. \]

Thus, non-reciprocity is manifested as a constructive and destructive interference between the conventional and magnetoelectric contribution to the materials optical response for $+k$ and $-k$, respectively.

### 1.3 Non-reciprocal optical effects

When a measured quantity remains invariant under the interchange of the source and the detector, the corresponding symmetry of the studied system is termed as reciprocity. Reciprocity in physics has a challenging definition. While Landau used the term as a synonym of time reversal symmetry, later it was generalized by also considering spatial symmetries of the studied system. A rigorous definition of reciprocity for general scattering processes has been recently given by Deák and Fülöp.

Specific to optical phenomena, among reciprocity-violating media let’s consider those which can distinguish between counter-propagating light beams irrespective of the polarization state of light. As a counter-example, we recall the well-known Faraday effect when the non-reciprocity holds for circularly and elliptically polarized light. In case of the Faraday-effect the reciprocity is violated for certain but not all polarizations, thus, in our terminology the corresponding media do not show directional optical anisotropy.

Although the presence of such reciprocity-violating directional anisotropy in the properties of bulk matter may seem strange and counter-intuitive, it has been recently verified in a large variety of low-symmetry materials. In a dissipative medium this directional anisotropy results in different strengths of absorption for beams traveling along opposite directions which is called
Figure 1.1: Schematic representation of direction-dependent light propagation in (a) transmission, (b) emission and (c) Bragg-scattering. (a) Forward and backward propagating beams distinguished by the medium are simultaneously shown. (b) Excitations by higher energy photons (blue arrow) decay via emission characterized by direction-dependent emission rates (red arrows). (c) Equal intensity for beams diffracted symmetrically to the direct beam is broken by directional anisotropy. The figures are reproduced from my work published in Ref. [22].

directional dichroism. Similar directional optical phenomena – schematically shown in Fig.1.1 – have already been observed for emission, [23, 24] absorption [25] and diffraction [26] of light in materials belonging to two different symmetry classes where the directional optical phenomena emerge in the two configurations described in the next two sections.

1.3.1 Optical magnetoelectric effect

The optical magnetoelectric effect (OME) was observed in systems with finite ferrotoroidic moment [11]—which can arise e.g. as the cross product of the static magnetization and electric polarization of the material, $\mathbf{T} = \mathbf{P} \times \mathbf{M}$—for light propagating along or opposite to the toroidal moment vector. Strong OME was first detected by Hopfield and Thomas in the absorption spectrum of excitons in the polar CdS with wurtzite structure. [25] Instead of reversing the light propagation, the sign of the toroidal moment was switched to be parallel and antiparallel to the propagation of light. A remarkable portion of the absorption was found to be odd function of both the magnetization and the electric polarization of the material as expected for OME. Later the same phenomenon was found for the polar ferrimagnet GaFeO$_3$ in the X-ray absorption of the core electron excitations [27] and for absorption due to intra-atomic d-d transitions over the visible-ultraviolet spectral range. [28, 29] Enhancement of OME in diffraction was also observed using a grating made of the same compound. [29] Metamaterials composed of two dimensional ferromagnetic islands with polar shape can also host OME in
Materials without spontaneous electric polarization and/or magnetization can show OME as well if a toroidal moment $T$ is induced by crossed static electric and magnetic fields, as was observed for the electronic $f-\bar{f}$ transitions of Er$^{3+}$ in Er$_{1.5}$Y$_{1.5}$Al$_5$O$_{12}$ \cite{31} and in Er-doped ferroelectric (Ba,Sr)TiO$_3$. \cite{32} Besides the usual case discussed above, spontaneous toroidal moment can also be present in antiferroelectric and/or antiferromagnetic compounds, whenever $t = \sum_i r_i \times m_i$ is finite \cite{33}, while $T$ can be vanishing. Here, $m_i$ and $r_i$ respectively stand for the $i$-th magnetic moment and its position ($i$ runs over spins in the magnetic unit cell). For example the spin texture present in skyrmion lattices \cite{34–36} can produce such $t$ toroidal moment without finite $T$.

Besides its manifestation in optical processes, similar directional anisotropy has been reported in diffusive electronic transport. The drain-source resistance of symmetric field effect transistors, when applying crossed magnetic field and electric field, showed difference for current flowing along or opposite to the toroidal moment. \cite{37} Directional anisotropy was predicted recently for the propagation of spin-waves in planar magnonic crystals with metallic over and dielectric under layers \cite{38, 39} and in an ultrathin Fe film on a W(110) surface. \cite{40} The latter was experimentally observed by spin-polarized electron energy loss spectroscopy. \cite{41} A heterostructure built of a thin Ni film evaporated on the surface of piezoelectric LiNbO$_3$ \cite{42} and even a single crystal of aluminium \cite{43} presents non-reciprocal surface acoustic wave propagation. In all cases ferrotoroidic moment was introduced parallel to the wave propagation by crossed magnetic field or spontaneous magnetization and electric polarization arising from the layered structure.

Except for the case of CdS, the previous examples for OME, detected in absorption/phase velocity/diffraction or in electric resistance, gave small relative directional differences in the range of $10^{-5} - 10^{-2}$. On the contrary, recent experiments on magnetoelectric multiferroic materials show a relative OME in the order of unity for intra-atomic $d-d$ transitions of CuB$_2$O$_4$ \cite{6, 44} in the near-infrared spectral region and in the electromagnon spectrum of various multiferroics (Ba$_2$CoGe$_2$O$_7$, \cite{46} Eu$_{0.55}$Y$_{0.45}$MnO$_3$, \cite{47} Gd$_{0.5}$Tb$_{0.5}$MnO$_3$, \cite{48} Sm$_{0.5}$La$_{0.5}$Fe$_3$(BO$_3$)$_2$, \cite{49} BiFeO$_3$, \cite{45} CaBaCo$_4$O$_7$, \cite{50} MnWO$_4$ \cite{51} and Ba$_3$NbFe$_5$Si$_2$O$_{14}$ \cite{52}) in the THz photon frequency range, which may eventually lead to their optical applications e.g. as magnetically controlled directional light switches. The schematic picture of such an optical diode based on a multiferroic crystal was proposed in Ref. \cite{45} and is shown in Fig. 1.2.
Figure 1.2: Schematic figure of an optical diode based on a magnetoelectric crystal as proposed in Ref. [45]. Red and green arrows correspond to the ordered electric polarization vectors and magnetic moments in the crystal. In perpendicular external magnetic and electric fields the transmission of counter-propagating light beams is different due to optical magnetoelectric effect of the collective magnetoelectric excitations. The transparent and absorbing directions can be switched by the reversal of either the magnetic field or the polarity of the applied $U$ voltage.

1.3.2 Magneto-chiral dichroism

The second type of optical directional anisotropy effect, the magneto-chiral dichroism (MChD) appears as a difference in the absorption or emission of chiral systems for light beams propagating parallel and antiparallel to an external magnetic field. The existence of MChD was first experimentally proved for a luminescent transition of the chiral Eu((±)tfc)$_3$ complex [23, 24] where the intensity of the emitted light slightly differed for propagation along or opposite to the external magnetic field. The effect was also shown in the infrared absorption of $\alpha$–NiSO$_4$·6H$_2$O [4] and in the enantioselective photochemical dissociation of chiral complexes. [53] Similar phenomenon, difference in phase retardation of counter-propagating light beams was found in chiral organic liquids. [5, 54] The emergence of MChD was also demonstrated in Bragg scattering. [26] The MChD in the absorption of microwave resonances of the chiral skyrmion host Cu$_2$OSeO$_3$ was extensively studied
both experimentally [55, 56] and theoretically [57]. The same compound presents MChD in the propagation of magnon modes also, [58] as does the chiral ferromagnet LiFe$_5$O$_8$ [59] as well. The effect also appears at much higher energies, in the hard X-ray spectrum of helical molecules containing magnetic ions. [60]

The electrical analog of MChD is the difference in conductivity of chiral systems for currents flowing parallel and antiparallel to the direction of an external magnetic field. Such electric magneto-chiral anisotropy was observed in helically distorted bismuth stripes [61] and also in chiral carbon nanotubes. [62]

In all these cases the directional anisotropy was rather weak corresponding to a relative difference of $10^{-8} - 10^{-2}$ in the studied quantities. On the other hand, similarly to the case of OME, multiferroic materials can show also a significant MChD effect in order of unity in both their infrared $d-d$ excitations (CuB$_2$O$_4$ [7]) and spin-wave absorption (Ba$_2$CoGe$_2$O$_7$, [63] Ca$_2$CoSi$_2$O$_7$, [64] Sr$_2$CoSi$_2$O$_7$, [64] CuFe$_{0.965}$Ga$_{0.035}$O$_2$, [65] MnWO$_4$ [51] and Ba$_3$NbFe$_3$Si$_2$O$_{14}$ [52]) spectra.

1.4 Fourier-transform far-infrared spectroscopy

Low-frequency Fourier-transform optical spectroscopy offers an excellent tool to investigate the magnetic field and temperature dependence of magnetic resonances and to sensitively detect the emergent non-reciprocal absorption effects. Due to the common usage of thermal light sources in optical spectroscopy, which radiate according to the black body radiation principle, the light intensity towards low frequencies is highly reduced, which makes spectroscopic studies in the far-infrared region challenging. In Fourier-transform spectroscopy the whole spectrum of radiation emitted by the source reaches the detector, as opposed to grating spectroscopy techniques commonly employed in the near infrared, visible, ultraviolet and X-ray regions, where a dispersive element is applied separating the light beam into monochromatic segments. The spectrum is recorded by subsequent measurements using these near-monochromatic segments of different wavelength. This feature leads to the so-called multiplex (or Felgett) advantage that partially recovers the signal to noise ratio due to the weakness of the source. For my far-infrared optical experiments I used the Martin-Puplett interferometer of the National Institute of Chemical Physics and Biophysics in Tallinn and the Michelson interferometer of the High Field Magnet Laboratory in Nijmegen, the technical details of the two setups are given in my master thesis [66] and in Ref. [64].
My research, presented in the subsequent chapters, aims at the better understanding of the non-reciprocal optical effects. First in Chapter 2 I investigate the symmetry conditions of directional anisotropy and propose some candidate systems likely host such non-reciprocal optical effects. In Chapter 3 I derive a sum-rule relation connecting the static magnetoelectric effect to the directional dichroism in the optical regime, thus explaining why the low frequency excitations of multiferroics present the strongest directional dichroism. In Chapter 4 I am going to present one realization of both the OME and the MChD effect on the example of the Co-based melilite crystal family, providing also an experimental verification of the sum rule. Finally, in Chapter 5 I will present a multiferroic system, TbFe$_3$(BO$_3$)$_4$, which despite its low symmetry compatible with directional optical anisotropy, and its static magnetoelectric effect, does not host such effects in the energy range of the magnon excitations.
Chapter 2

Symmetry considerations on directional anisotropy

Directional anisotropy, i.e., different propagation of waves or particles along opposite directions, is a highly unusual and counterintuitive phenomenon. In the course of geometrical optics, one of the main principles is Helmholtz’s reciprocity theorem \[1-3\] stating that counter-propagating light rays follow the same path and experience the same refractive index. However, in geometrical optics the medium is supposed to be isotropic and invariant under the reversal of the flow of time. When these fundamental symmetries are violated, light propagation along opposite directions is no longer granted to be identical. In this chapter I will discuss how directional anisotropy is related to the symmetry of matter and can be predicted based on the spatial and magnetic structure of the media. The train of thought follows my work published in Ref. [22].

In classical electrodynamics light-matter interaction possesses time reversal \[67\] (\(\tau\)) and full \(O(3)\) spatial symmetry, either of which is only violated when the weak interaction of matter is also considered. Since the weak interaction rarely manifests itself in condensed matter systems, this means that transformation of the whole optical experiment—light source-sample-detector system—by any symmetry operation of \(\tau \otimes O(3)\) must not affect the interaction process when the weak interaction is neglected.

Therefore, when studying the optical properties of magnetic crystalline media only the crystallographic and magnetic structure of matter can introduce constraints on the symmetry of the measured optical quantities. Using Neumann’s principle \[8\] these constrains can provide relations between the tensor elements describing the optical response such as elements of transmittance and reflectivity matrices. These relations can be experimentally probed by changing the polarization or propagation direction of light. We
focus on such cases when the equality of these tensor components for forward
and backward propagation is broken by the low magnetic symmetry of the
material. Thus, the realization of such directional anisotropy phenomena
requires that every symmetry operations, which could convert any of the op-
tical processes into their reversed pairs, are missing from the magnetic point
group of the crystal.

According to our definition, directional anisotropy is allowed for a given
axis of propagation, if no symmetry operation of the crystal can transform
a light beam (of any polarization) traveling along this axis into a counter-
propagating one without changing its polarization state. This means that
the path of the electric polarization vector determines the same curve in the
laboratory frame upon forward and backward propagation.

2.1 Crystal symmetries compatible with di-
rectional anisotropy

As a necessary condition, the material must lack spatial inversion and time
reversal symmetries because they convert counter-propagating beams with
the same linear polarization into each other. To systematically determine
the conditions of directional anisotropy in a crystal one has to consider each
symmetry element of the corresponding magnetic point group. Let us take
a beam with arbitrary elliptical polarization state propagating along the
z-axis. Since the electric displacement and magnetic flux density vectors
\( D \) and \( B \), respectively lie in the \( xy \)-plane one only needs to treat those
orthogonal transformations which leave this plane invariant. In crystals these
are the \( n \)-fold proper \((n)\) and improper \((\pi)\) rotations around the z-axis for
\( n = 1, 2, 3, 4 \) and \( 6 \) and around an axis lying in the \( xy \)-plane for \( n = 1 \) and
\( 2 \). All of these operations can be combined with the reversal of time which
is hereafter denoted by a prime (\( ' \)). In our convention an improper rotation
means a proper rotation combined with spatial inversion, i.e. the spatial
inversion and mirror plane symmetries are noted as \( T \) and \( \bar{2} \), respectively.

As long as the propagation of unpolarized light is considered, the nec-
essary and sufficient condition for the presence of a directional anisotropy
effect along the z-axis is that no symmetry of the system can connect the op-
posite propagation directions, i.e. transform light \( \mathbf{k} \uparrow \uparrow \mathbf{z} \) vector to \( -\mathbf{k} \downarrow \downarrow \mathbf{z} \).
Half of the transformations listed in the previous paragraph conserve the
propagation direction, since we have the freedom to combine a spatial opera-
tion with time reversal, which converts a propagation-reversing symmetry
to a propagation-conserving one and vice versa. Proper rotations \((n)\) and
improper rotations combined with time reversal ($\pi'$) around the z-axis meet this criterion for any $n \in \{1, 2, 3, 4, 6\}$. Besides that $2$ and $2'$ rotations around an axis perpendicular to the z-direction also conserve the propagation direction. In magnetic point groups containing only these propagation-conserving operations — together with any other transformations which do not leave $xy$-plane invariant—the propagation along the $+z$ and $-z$ directions can be different not only for unpolarized light but also for other unpolarized or scalar waves (e.g. acoustic waves) as well as for unpolarized beams of particles.

Next, we also take the polarization state of light into account, because there can be some propagation-reversing operations which also alter the polarization state of light (for each polarization) and thus allow directional optical anisotropy. However, this will only slightly affect the results obtained above. Among the rotations around the $z$-axis only $\pi$ and $\pi'$ reverse the propagation of light. Both transformations rotate the axes of the polarization ellipse by $\frac{2\pi}{n}$. While $\pi'$ transposes clockwise and counterclockwise circulation of the polarization, $\pi$ preserves the sense of circulation in the laboratory frame. Since the direction of propagation is reversed, $\pi'$ will preserve and $\pi$ will change the the sense of circulation in the frame of the light beam. For $n = 1$ and $2$, $\pi'$ connects every elliptical polarization state with its counter-propagating pair, and $\pi$ does the same for linearly polarized states. Thus, both prohibit directional optical anisotropy (in our term), since the propagation direction is reversed and the polarization in the light frame is kept intact at least for specific polarizations. For $n = 3$ the $n$-times repetition of $\pi'$ and $\pi$ results in $1'$ and $\mathbf{1}$, respectively, and for $n = 6$ the $2$-times repetition of $\pi'$ and $\pi$ gives $2'$ and $2$, respectively, which all forbid directional anisotropy. In contrast, for $n = 4$ no power of $\mathbf{1}$ can convert light beams with elliptical polarization to their oppositely propagating pair. For $4'$ the same is true except for the right- and left handed circularly polarized states which are transformed into their counter-propagating pair.

Among the operations around an axis lying in the $xy$-plane only $1', \mathbf{1}, 2$ and $2'$ can reverse the propagation direction and preserve the polarization state of the light beam at least for some specific (e.g. linear) polarizations. For $n = 2l$ even integers the $l$-times repetition of an $n$-fold rotation (denoted as $(n)^l$) gives 2 and $(\pi')^l$ results either in 2 or $2'$ depending on the parity of $l$. For $n = 4l$, $(n')^{2l} = (\pi)^{2l} = 2$ and for $n = 2l + 1$, $(n')^n = 1'$ and $(\pi)^n = \mathbf{1}$. Therefore, the presence of $2l, 2l', 4l', 4l, (2l + 1)'$ or $2l + 1$ rotations around an axis within the $xy$-plane prohibits directional anisotropies along the $z$-axis. Rotations around arbitrary axes, which are neither parallel nor perpendicular to $z$, cannot generally connect opposite propagation directions along the $z$-axis.
To conclude this analysis, almost all symmetry operations which reverse the direction of the light propagation retain at least one polarization state and hereby they cannot be present in the magnetic point groups of crystals exhibiting directional anisotropy. The only exception is 4 which allows directional anisotropy for any light polarization except for unpolarized light where the difference cancels out. It is also important to emphasize that in any crystal lacking the time reversal and spatial inversion symmetries, the directional anisotropy can emerge for any arbitrary direction of wave propagation except for high symmetry axes.

2.2 Classification of directional anisotropy based on symmetry

Table 2.1 lists all crystallographic magnetic point groups except those which contain the time-reversal or spatial inversion symmetry. In the table I indicate which symmetry groups support directional anisotropy along certain high-symmetry axes. In some magnetic point groups the presence of directional anisotropy can be straightforwardly demonstrated by showing a static symmetry breaking vectorial quantity of the material which transforms under the symmetry elements of the group in the same way as the $k$ propagation vector of light.

A static toroidal moment ($T$ or $t$) transforms under all possible symmetry operations identically to the wave vector of light since the latter is the cross product of the oscillating electric and magnetic components. Therefore, systems with finite toroidal moment vector allow directional anisotropy for beams propagating parallel or antiparallel to this vector and the corresponding effect is termed as optical magnetoelectric effect of toroidal origin (OME). The magnetic point groups compatible with $T$ – denoted by $T$ in Table 2.1 – are subgroups of the symmetry group of a perpendicular magnetic and electric field vector, $2'nn'1$, where the electric field is parallel to the 2' axis, the magnetic field is perpendicular to the mirror plane $m$ and $T$ points perpendicular to the mirror plane $m'$. In the notation of the magnetic point groups the international convention is followed, where $m$ stands for mirror plane symmetry. The toroidal moment $t$ can arise without the presence of electric polarization and magnetization, thus, $t$ is compatible with higher symmetry point groups than $T$. Indeed, $t$ can exist in the same point groups where a general time-reversal odd polar vector can appear. In the literature $t$ is usually called toroidal moment, defined according to

$$t = \sum_i e_i r_i \times S_i,$$  \hspace{1cm}(2.1)
Table 2.1: Crystallographic magnetic point groups and possible configurations for directional anisotropy (DA). Point groups containing the ‘1’ time reversal or \(\mathbb{T}\) spatial inversion operation are omitted. After the international symbol of each point group the symmetry allowed magnetic structure (F - ferromagnetic, AP - antiferromagnetic) is indicated. The axis of the rotation or the normal of the mirror plane listed first in the international notation of the point group is denoted as PA (principal axis). The potential directional anisotropy configurations are listed for wave propagation parallel and perpendicular to the principal axis as \(\parallel\) to PA and \(\perp\) to PA, respectively. Here i) T and t, ii) MC, and iii) P mean the directional anisotropy effects emerging in i) ferrotoroidic materials for propagation parallel to the toroidal moment \(\mathbb{T}\) and \(\mathbb{t}\), ii) in chiral systems for light traveling along the magnetic field, and iii) in point groups, where none of the group elements is combined with the time reversal for propagation along the ferroelectric polarization, respectively. X denotes cases where directional anisotropy can also be present but it cannot be characterized by a static vector quantity. Several examples of magnetoelectric materials belonging to the given magnetic point group are elements of the 5th and 10th columns, where \(B_\alpha\) stands for an external magnetic field pointing to the \(\alpha\) crystallographic direction. This collection of materials and their magnetic point groups extends the similar lists of former studies. [22, 68-73]

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>International notation</th>
<th>DA (\parallel) PA</th>
<th>DA (\perp) PA</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>(\alpha) (AF)</td>
<td>(\gamma) (AF)</td>
<td>(\nu) (AF)</td>
<td>(\tau) (AF)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(\alpha) (AF)</td>
<td>(\gamma) (AF)</td>
<td>(\nu) (AF)</td>
<td>(\tau) (AF)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>(\alpha) (AF)</td>
<td>(\gamma) (AF)</td>
<td>(\nu) (AF)</td>
<td>(\tau) (AF)</td>
</tr>
<tr>
<td>Cubic</td>
<td>(\alpha) (AF)</td>
<td>(\gamma) (AF)</td>
<td>(\nu) (AF)</td>
<td>(\tau) (AF)</td>
</tr>
</tbody>
</table>
while $T$ corresponds to

$$T = \left( \sum_i e_i r_i \right) \times \left( \sum_i S_i \right) = P \times M. \quad (2.2)$$

In the case of crystals these are the subgroups of $n/m'm'm$ and $\pi'2'm$ where $t$ is parallel to the principal axis and $n = 4$ or $6$. Since a spontaneous, nondissipative electric current $[164]$, present in e.g. superconductors, has the same symmetry properties as $t$, they belong to the same 31 crystallographic magnetic point groups. These groups are labeled with $t$ in Table 2.1.

Chiral systems only possess proper rotational symmetries, which may be combined with the reversal of time. All of these operations transform the axial vector of the magnetic field (or spontaneous magnetization) and the polar wave vector in the same way. Therefore, in chiral systems with a time-reversal odd axial vectorial order parameter, such as magnetization, light propagation along or opposite to this vector cannot be connected by symmetry. The corresponding directional anisotropy is the so-called magneto chiral dichroism (MChD), indicated by MC in Table 2.1.

Additionally to the already known cases of OME and MChD, I found new possibilities to realise directional anisotropy. If a polar magnetic point group contains only symmetry elements which are not combined with time-reversal then these operations transform the vector of electric polarization or temperature gradient, both even in time reversal, in the same way as the wave vector being odd in time reversal. In this case the presence of a static polarization/temperature gradient makes the wave propagation along or opposite to these vectorial quantities inequivalent. This potential directional anisotropy effect, denoted by $P$ in Table 2.1, has not been studied either theoretically or experimentally so far.

Please note that whenever symmetry permits directional anisotropy of either T-, MC- or P-type, then $t$-type directional effect can also emerge. Nevertheless, the distinction between these cases is meaningful as the microscopic physical origin of these directional effects can be different. Besides these cases I found additional situations when the symmetry condition for directional anisotropy cannot be related to any static vectorial quantity which transforms in the same way as the wave vector. These point groups are marked with an $X$ in Table 2.1.

Except for the magnetic point group $\mathbf{T}$, all the cases of directional anisotropy listed in Table 2.1 also have validity for other processes than light propagation. Symmetry elements of these groups cannot reverse the propagation direction and, thus, allow directional anisotropy for propagation of electrons, neutrons, acoustic- and spin-waves, and in electric or heat conduction.
In some other groups directional anisotropy is conceivable but only for polarized light, spin polarized neutron and electron beams or any transversal wave. These cases can be determined by systematical checking whether the propagation-reversing operations can preserve the polarization state. Specific to light propagation, I found that $4$ is the only additional point group supporting directional optical anisotropy.

Another approach to study directional optical anisotropy is the symmetry analysis of the optical response functions. Due to its simultaneous time-reversal and spatial inversion breaking nature, optical directional anisotropy can only be produced by the bilinear magneto-electric tensor when dipole approximation appropriately describes the light-matter interaction. The non-vanishing elements of this tensor can be identified by the symmetry analysis of the given material. For the static magneto-electric tensor the result of such analysis based on magnetic point groups can be found in the literature. [9] While the static magneto-electric tensor can only contain time-reversal odd elements, the dynamic one may have time reversal even part as well. Indeed the natural optical activity of chiral molecules with random orientations exclusively comes from the time reversal even part of the dynamic magneto-electric susceptibility. [17] Therefore, the symmetry dictated form of the dynamic magneto-electric tensor needs to be included in the constitutive relations in order to solve Maxwell's equations and check the presence of directional anisotropy. This approach is specific to optics and its validity is restricted to the dipole approximation of light-matter interaction. Considering compounds with cubic magnetic point groups, in dipole order no directional anisotropies can be present since the magneto-electric tensor is proportional to the unit tensor. However, taking into account higher order terms described e.g. by electric quadrupole tensor, the symmetry allowed directional anisotropy along the threefold axis shown in Table 2.1 can be reproduced. Therefore the present approach provides a more general framework to address the question of directional anisotropies in crystalline solids.

In conclusion, using symmetry considerations possible configurations were determined, where $\pm k$ direction-dependent optical phenomena can emerge. Besides the conventional OME and MChD effects, a third potential directional anisotropy effect was predicted when the wave propagation is parallel to the electric polarization in materials whose symmetry groups do not contain any symmetry operation involving time reversal. With one exception, all the listed configurations allow non-reciprocity for any transport phenomenon, particle or wave propagation. I identified each crystallographic magnetic point group which can host directional anisotropies providing a key for the systematic investigation of candidate materials. I also propose a large collection of crystals where these effects are expected to emerge.
Chapter 3

Magnetoelectric sum rule

The magnetoelectric coupling between local magnetic and electric dipole moments in multiferroic materials offers a fundamentally new path for data storage. A future magnetoelectric device could combine the best qualities of ferroelectric and magnetoresistive memories: fast low-power electrical read and write operation inherently coupled to a non-destructive non-volatile magnetic data storage unit. [168, 169] This potential application motivates the research of multiferroic crystals and makes it one of the most intensively studied fields of contemporary solid state physics. [168–173]

The same magnetoelectric coupling appears in the optical regime manifested in the difference of refractive indices of counter-propagating light beams. Thus, materials originally designed for the prospect in their static magnetoelectric properties can also be investigated by means of optical spectroscopy in order to develop optical diodes, transmitting light in one, but not in the opposite direction. The schematic picture of such an optical diode based on a multiferroic crystal is shown in Fig 1.2. In this chapter, following my results published in Ref. [174], I will derive a sum rule formula relating the difference in light absorption observed for counter-propagating beams to the static magnetoelectric susceptibility. I will also show some well known examples of sum rule relations for the electric and magnetic responses, motivating the hunt for an analogous expressions of the magnetoelectric susceptibility.

3.1 Kramers-Kronig relation

The Kramers-Kronig relation, [175, 176] also known as the Hilbert transformation of complex functions, connects the real (ℜ) and imaginary (ℑ) parts
of a causal frequency dependent linear response function:
\[
\Re \chi_p(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\Im \chi_p(\omega')}{\omega' - \omega} \, d\omega' \
\mbox{and}\quad \Im \chi_p(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\Re \chi_p(\omega')}{\omega' - \omega} \, d\omega',
\] (3.1)
where \( \mathcal{P} \) stands for the Cauchy principal value integral. The \( \chi(\omega) \) susceptibility corresponds to a linear and causal response function in the time domain.

In many cases, either the real or the imaginary part of \( \chi(\omega) \) can be determined experimentally and the Kramers-Kronig transformation is extensively used to obtain the entire complex response function. \[177\]

### 3.2 The connection between static and dynamic response

In the static limit of \( \omega = 0 \), the equation 3.1 is simplified to the following form, which shows close similarity with sum rules:
\[
\Re \chi(\omega = 0) \equiv \chi(0) = \frac{2}{\pi} \mathcal{P} \int_{0}^{\infty} \frac{\Im \chi(\omega)}{\omega} \, d\omega, \quad (3.2)
\]
\[
\Im \chi(\omega = 0) \equiv 0 = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\Re \chi(\omega)}{\omega} \, d\omega. \quad (3.3)
\]
Equation 3.2 shows that the static response of a system is fully determined by the corresponding dynamical susceptibility and the frequency denominator on the right-hand side indicates the enhanced role of low-energy excitations in the static susceptibility.

Typically, the dynamic susceptibility cannot be measured down to arbitrarily low frequencies and there is a missing spectral window between the static and the finite-frequency experiments. In such situations, the measured data are usually extrapolated, based on an apriori assumption. When \( \Im \chi(\omega) \) is the measured component of the dynamic response, the consistency of such extrapolations can be verified using Eq. 3.2 and possible discrepancies imply the presence of additional excitations in the low-frequency region uncovered by the experiment.

#### 3.2.1 Electric response

Applying Eq.3.2 to the uniform electric response of the system and using \( \omega \chi^{ee}(\omega) = i\sigma(\omega) \) relation between the complex electric susceptibility \( \chi^{ee}(\omega) \) and electrical conductivity \( \sigma(\omega) \) one gets \[178, 179\]
\[
\sigma(0) = \frac{2}{\pi} \mathcal{P} \int_{0}^{\infty} \frac{3\sigma(\omega)}{\omega} \, d\omega = -\frac{2}{\pi} \mathcal{P} \int_{0}^{\infty} \Re \chi^{ee}(\omega) \, d\omega \quad (3.4)
\]
for the static conductivity ($i$ is the imaginary unit). For instance, in the case of insulators this means that the average value of the real part of the $\varepsilon(\omega) = 1 + \chi^{\text{re}}(\omega)$ dynamical relative permittivity is 1. Similarly, it can be shown that the static $\varepsilon(0)$ permittivity is mainly determined by the real part of the low-frequency conductivity of the system

$$\varepsilon(0) - 1 = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\Im \chi^{\text{re}}(\omega)}{\omega} d\omega = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\Re \sigma(\omega)}{\omega^2} d\omega$$

(3.5)
due to the $\frac{1}{\omega^2}$ cutoff of the integrand.

A common example is the dielectric permittivity of semiconductors, which is usually larger for compounds with smaller energy gap and can be considerably affected by the contributions from low-energy phonon modes. A particularly strong enhancement is found in quantum paraelectrics due to the presence of soft polar phonon modes. [180, 181] Besides low-energy or soft modes, in materials with ferroic orders, the $ac$ susceptibility related to the domain dynamics can also influence the static response.

### 3.2.2 Magnetic response

When measuring the dynamic magnetic response, one is interested in the magnetic field dependence of the magnetization current density, $J_m$. However, at high frequencies it gets dominated by the displacement current term, $J_p = \partial \mathbf{P}/\partial t$. $J_p$ is generated by the electric field induced by the time derivative of the magnetic induction used as external stimulus in the experiment. Consequently, the definition of $\mathbf{M}^{\mu}$ as the rotation of $J_m$ does not correspond to the spatial density of the macroscopic magnetization any more. Since $\nabla \times J_m$ is limited by the size of the sample, a simple calculation yields that in the frequency regime of the visible optics already the $J_m \ll J_p$ limit is reached. [182]

Therefore, at high enough frequencies the magnetic susceptibility loses its physical meaning and Eq.3.2 needs to be slightly reformulated. Using the $\mu(\omega) = 1 + \chi^{mm}(\omega)$ relation only up to an $\omega_1$ frequency limit,

$$\chi^{mm}(0) = \chi^{mm}(\omega_1) + \frac{2}{\pi} \mathcal{P} \int_0^{\omega_1} \frac{\Im \chi^{mm}(\omega)}{\omega} d\omega.$$  

(3.6)

The frequency limit should be chosen so that at $\omega_1$ the magnetic susceptibility is still meaningful, but already can be considered zero for the complex $z$ frequencies when $|z| = \omega_1$ on the upper complex half-plane ($\Im z \geq 0$). This practically means that $\omega_1$ should be much larger than the highest para- or ferromagnetic resonance frequency of the medium. [182]
If the material under study has only magnetic resonances at low frequencies, the optical absorption coefficient in this frequency domain is determined by the imaginary part of the magnetic susceptibility:

\[
\alpha(\omega) = \frac{2\omega}{c} \Im N(\omega) \approx \frac{\omega \sqrt{\varepsilon^\infty}}{c} \Im \chi^{mm}(\omega),
\]

where the

\[
N(\omega) = \sqrt{\varepsilon(\omega)/\mu(\omega)} = \sqrt{\varepsilon^\infty}(1 + \chi^{mm}(\omega)) \approx \sqrt{\varepsilon^\infty} \left( 1 + \frac{\chi^{mm}(\omega)}{2} \right)
\]

relation was used. Here \(N(\omega)\) is the index of refraction, and the dielectric permittivity is considered to be real \(\varepsilon^\infty\) in the studied low-frequency region. This results in

\[
\chi^{mm}(0) \approx \frac{2\varepsilon_0}{c} \frac{\pi}{\sqrt{\varepsilon^\infty}} \mathcal{P} \int_0^{\omega_1} \frac{\alpha(\omega)}{\omega^2} d\omega,
\]

indicating the dominant role of low-frequency magnetic excitations in the static magnetic susceptibility. Since the absorption is non-negative, \(\alpha(\omega) \geq 0\), Eq. 3.9 can result only in paramagnetic static susceptibility.

However, the Kramers-Kronig formula in the above discussed form only holds for the local magnetic response. In case of non-local response, the separation of the spatial variation of the magnetization and the temporal variation of the electric polarization is arbitrary. Thus, to form a sum rule, both the electric and magnetic responses need to be considered. [178] Diamagnetism, e.g., in superconductors, may also be related to the spatially non-uniform magnetic response.

### 3.2.3 Magnetoelectric response

In multiferroic materials the coupling between the electric polarization \(P^\omega\) and the magnetization \(M^\omega\) in dipolar order can be phenomenologically described by the magnetoelectric susceptibility tensors \(\chi^{me}(\omega)\) and \(\chi^{em}(\omega)\). The \(\Delta M^\omega\) contribution to the magnetization is generated by an oscillating electric field \(E^\omega\), and \(\Delta P^\omega\) is the polarization induced by an oscillating magnetic field \(H^\omega\), respectively:

\[
\Delta M_\gamma^\omega = \sqrt{\frac{\varepsilon_0}{\mu_0}} \chi^{me}_{\gamma\delta}(\omega) E_\delta^\omega \quad \text{and} \quad \Delta P_\delta^\omega = \frac{1}{c} \chi^{em}_{\delta\gamma}(\omega) H_\gamma^\omega.
\]

Here \(\varepsilon_0\) and \(\mu_0\) are the vacuum permittivity and permeability, respectively, and \(c\) is the speed of light in vacuum, while \(\gamma\) and \(\delta\) stand for the Cartesian
coordinates. The two cross-coupling tensors are connected by the \{\ldots\}' time-reversal operation according to \(\{\chi^{me}_{\gamma\delta}(\omega)\}' = -\chi^{em}_{\delta\gamma}(\omega)\).

Although the static magnetoelectric susceptibility \(\chi^{me}_{\gamma\delta}(0)\) is always antisymmetric to the time reversal, this is not true for the dynamic response. In fact, the time reversal even part of the diagonal \(\chi^{me}_{\gamma\gamma}(\omega \neq 0)\) tensor element is responsible for the natural optical activity in chiral materials. [17, 183]

Moreover, manifestation of magnetically induced chirality has been observed recently in the spin excitations of multiferroic Ba2CoGe2O7. [63]

As seen in Chapter 2, a broad class of materials simultaneously lacking the spatial inversion and the time reversal symmetries are good candidates for directional anisotropy. In fact, it has been indeed observed that various materials [11, 22, 184–186] including multiferroic compounds, can differentiate between counter-propagating electromagnetic waves, since the time reversal odd part of the ME susceptibility is manifested as a non-reciprocal term in their refractive index. However, it is hard to derive the exact form of the refractive index for most of these materials due to their low symmetries. Moreover, the propagating solutions of the Maxwell equations are usually elliptically polarized in these systems. Nevertheless, when measuring the transmission of sufficiently thin samples with linearly polarized incident beams, the polarization of light is nearly preserved during propagation through the specimen and the index of refraction can be approximated as

\[
N^\pm(\omega) \approx \sqrt{\varepsilon_{\delta\delta}(\omega)\mu_{\gamma\gamma}(\omega)} \pm \frac{1}{2} \left[ \chi^{me}_{\gamma\delta}(\omega) - \{\chi^{me}_{\gamma\delta}(\omega)\}' \right]. \tag{3.11}
\]

Here \(N^\pm\) stands for the refractive indices of waves propagating in opposite directions (\(\pm k\)). The \(\delta\) and \(\gamma\) coordinate axes are parallel to the direction of the electric (\(\mathbf{E}^e\)) and magnetic (\(\mathbf{H}^e\)) fields of light, respectively, while \(\varepsilon_{\delta\delta}(\omega)\) and \(\mu_{\gamma\gamma}(\omega)\) are diagonal components of the complex relative permittivity and permeability tensor. In some special cases, the exact solutions of Maxwell’s equations can be derived when the propagating solutions are either linearly or circularly polarized. [64]

The difference in the imaginary part of the \(N^+\) and \(N^-\) refractive indices gives rise to a difference in the absorption coefficients of counter-propagating waves, termed as directional dichroism:

\[
\Delta\alpha(\omega) = \alpha_+(\omega) - \alpha_-(\omega) = \frac{2\omega}{c} \Im(\chi^{me}_{\gamma\delta}(\omega) - \{\chi^{me}_{\gamma\delta}(\omega)\}'). \tag{3.12}
\]

A direct comparison between such directional dichroism spectra and the static magnetoelectric data is possible whenever the linear polarization of the incident light is nearly preserved during the propagation through the
magnetoelectric medium. Therefore, we restrict our study to these cases captured by Eq. 3.11. In the next section I will show that Eq. 3.11 can even be applied for materials where the solutions of the Maxwell equations are circularly polarized waves if a polarization independent detection scheme is used.

In Eq. 3.11 we have also neglected the longitudinal component of the polarization induced e.g. by magnetization perpendicular to the light propagation. Thus, additional terms in the refractive index, which are higher-order products of off-diagonal tensor components like $\chi_{\delta\beta}^{\text{me}} e_{\beta\gamma} / e_{\delta\beta}$ or $\chi_{\beta\delta}^{\text{me}} \mu_{\beta\gamma} / \mu_{\beta\delta}$ are neglected. Here $\beta$ denotes the axis of the light propagation.

**Optical measurement of the magnetoelectric tensor elements in the case of circular light polarization eigenstates**

Following Ref. [64], let’s consider the highest symmetry case, when magneto-chiral dichroism can emerge, namely the magnetic point group $4_{2}^{1}2_{1}^{1}d$. Since the four-fold symmetry forbids linear dichroism in this chiral group for light propagation along the $z$ axis, the light polarization eigenstates will be circular. The four indices of refraction for the two opposite propagation directions ($\pm$) and polarization states ($l/r$) are:

\[
N_{\pm}^{l} = \sqrt{(\varepsilon_{xx}^{\prime} \pm i \varepsilon_{yy}^{\prime})(\mu_{xx}^{\prime} \pm i \mu_{yy}^{\prime})} + i \chi_{xx}^{\text{me}} \pm \chi_{yx}^{\text{me}} \text{ and } (3.13)
\]

\[
N_{\pm}^{r} = \sqrt{(\varepsilon_{xx}^{\prime} \pm i \varepsilon_{yy}^{\prime})(\mu_{xx}^{\prime} \pm i \mu_{yy}^{\prime})} - i \chi_{xx}^{\text{me}} \pm \chi_{yx}^{\text{me}}. \quad (3.14)
\]

Here one and two primes on the dielectric permittivity and magnetic permeability tensor components indicate invariance and antisymmetry of the given element upon time-reversal, respectively, while for the magnetoelectric tensor the assignment is the opposite, one prime denotes the time reversal antisymmetry. The imaginary unit is again denoted by $i$. Using all the four indices of refraction, the time reversal antisymmetric $\chi_{yx}^{\text{me}}$ tensor element can be expressed as

\[
\chi_{yx}^{\text{me}} = \frac{(N_{+}^{l} - N_{-}^{l}) + (N_{+}^{r} - N_{-}^{r})}{4}. \quad (3.15)
\]

However, $\Im \chi_{yx}^{\text{me}}$ can also be experimentally determined by measuring the directional dichroism spectrum for linear polarization of light. When using linearly polarized incident beam and polarization independent detection, and also neglecting the polarization dependence of reflection losses, the transmitted intensity reads as

\[
I_{\pm} = \frac{I_0}{2} \left( e^{-\alpha_{\pm}^{l}d} + e^{-\alpha_{\pm}^{r}d} \right) = I_0 e^{-\frac{\alpha_{\pm}^{l} + \alpha_{\pm}^{r}}{2}d} \text{ch} \left( \frac{\alpha_{\pm}^{l} - \alpha_{\pm}^{r}}{2}d \right). \quad (3.16)
\]
irrespective of the polarization plane of the incoming wave. Here $I_0$ is the incoming intensity after reflection losses and $d$ is the thickness of the sample. Comparing the transmitted intensity measured for the opposite propagation directions, one can define an effective $\Delta \alpha_{\text{eff}} = -\ln(I_+/I_-)/d$ directional absorption difference. With this definition in first order of the sample thickness

$$\Delta \alpha_{\text{eff}} \approx \frac{4\omega}{c} \Im \chi^{\text{me}}_{yx} + \left(\frac{2\omega}{c}\right)^2 \Re \chi^{\text{me}}_{xx} \Re \left[ \sqrt{\varepsilon_{xx} \mu_{xx}} \left(\frac{\varepsilon''_{xx}}{\varepsilon'_{xx}} + \frac{\mu''_{xx}}{\mu'_{xx}}\right)\right] d. \quad (3.17)$$

The product of $\Re \chi^{\text{me}}_{xx}$ and $\Re \left[ \sqrt{\varepsilon_{xx} \mu_{xx}} \left(\frac{\varepsilon''_{xx}}{\varepsilon'_{xx}} + \frac{\mu''_{xx}}{\mu'_{xx}}\right)\right]$ corresponds to the cascade effect of natural and magnetic circular dichroism. As it was shown in the absorption of chiral crystals, \cite{4} for samples with reasonable thickness this contribution is negligibly small compared to the magneto-chiral dichroism coming from $\Im \chi^{\text{me}}_{yx}$. This is the consequence of the fact that the off-diagonal elements of the dielectric permittivity and the magnetic permeability tensors are usually much smaller than the diagonal ones. Thus the magnetoelectric sum rule in Eq. 3.18 can be directly applied even for the high symmetry chiral crystals either in the thin sample approximation or by measuring the transmission for different sample thicknesses and extrapolating the effective absorption coefficient to zero sample thickness.

In case of low-symmetry, e.g. orthorhombic crystal, the linear birefringence mainly originates from the anisotropy of $\varepsilon$. Therefore the initial linear polarization of light is nearly preserved for larger thicknesses also, hence Eq. 3.11 is applicable for thick samples as well.

**The magnetoelectric sum rule**

Application of the Kramers-Kronig relations to the linear magnetoelectric susceptibility gives rise to sum rules analogous to Eqs. 3.4, 3.5 and 3.9. Usually $\chi^{\text{me}}(\omega)$ can hardly be determined from the optical quantities of the material, since typically the different contributions to the refractive index coming from the dielectric permittivity, the magnetic permeability and the magnetoelectric susceptibility cannot be separated. Consequently, in their generally valid forms Eqs. 3.2 and 3.3 have little practical use for the magnetoelectric susceptibility.

However, using Eq. 3.12 the general sum rule in Eq. 3.2 can be reformulated in a more specific way, which directly connects the static magnetoelectric effect to the directional dichroism spectrum:

$$\chi^{\text{me}}_{\gamma\delta}(0) = \frac{c}{2\pi} \mathcal{P} \int_0^\infty \frac{\Delta \alpha(\omega)}{\omega^2} d\omega. \quad (3.18)$$
According to this sum rule the static magnetoelectric effect is mostly governed by the directional dichroism of low-energy excitations, since the absorption difference, $\Delta \alpha$, is suppressed by the $\omega^2$ denominator at higher frequencies.

A similar sum rule was recently developed for magnetoelectric media by generalizing the Lyddane-Sachs-Teller relation. However, its applicability to multiferroic materials with low symmetry is again limited, because it requires all elements of the magnetoelectric tensor to be determined experimentally.

In Section 3.2.4 I also derive the magnetoelectric sum rule using the Kubo formula and show that only the time reversal odd part of $\chi^{me}(\omega)$ contributes to the integral in Eq. 3.2. Thus, in the sum rule the dynamic magnetoelectric susceptibility can indeed be replaced by the directional absorption difference.

### 3.2.4 Derivation of the magnetoelectric sum rule from the Kubo formula

Using Eqs. 1.7 and 3.12 one can reproduce the magnetoelectric sum rule:

$$\chi^{me}_{\gamma \delta}(0) = \frac{2V_c}{\hbar} \sqrt{\frac{\mu_0}{\varepsilon_0}} \sum_m \frac{\Re(\langle 0 | M_\gamma | m \rangle \langle m | P_\delta | 0 \rangle)}{\omega_m}$$

$$= \frac{2V_c}{\hbar} \sqrt{\frac{\mu_0}{\varepsilon_0}} \sum_m \Re \langle 0 | M_\gamma | m \rangle \langle m | P_\delta | 0 \rangle \int_0^\infty \frac{\delta(\omega - \omega_m) - \delta(\omega + \omega_m)}{\omega} d\omega$$

$$= \frac{c}{2\pi} \mathcal{P} \int_0^\infty \frac{\Delta \alpha(\omega)}{\omega^2} d\omega.$$  \hspace{1cm} (3.19)

In this derivation I used that in case of positive $\omega_m$ one gets $\int_0^\infty \frac{\delta(\omega + \omega_m)}{\omega} d\omega = 0$.

Since $\mathcal{P} \int_0^\infty \frac{1}{\omega - \omega_m} d\omega = 0$, the time-reversal symmetric (imaginary) part of the magnetoelectric matrix element product does not contribute to the frequency integral in Eq. 3.2, and instead of $\Im \chi^{me}_{\gamma \delta}(\omega)$ one can use the $\frac{c}{2\pi} \Delta \alpha(\omega) = \Im (\chi^{me}_{\gamma \delta}(\omega) - \{\chi^{me}_{\gamma \delta}(\omega)\}'$ absorption difference on the integral side of the magnetoelectric sum rule.

In conclusion, in this chapter I have shown that similarly to the more familiar electric and magnetic responses (Eqs. 3.4, 3.5 and 3.9), the static magnetoelectric susceptibility can also be connected to the integral of the corresponding low-frequency dynamic quantity, namely to the absorption difference observed for counter-propagating electromagnetic waves.
Chapter 4

Magnetolectric resonances and directional dichroism in Co-based melilite crystals

In this chapter I am going to report about the observation of directional dichroism in the low-frequency excitations of the Co-based magnetoelectric melilite crystal family. As shown in Table 2.1, in external magnetic field the magnetic symmetry of these crystals —Ba$_2$CoGe$_2$O$_7$, Ca$_2$CoSi$_2$O$_7$ and Sr$_2$CoSi$_2$O$_7$— is low enough to exhibit various types of directional dichroism. Their static magnetoelectric properties—magnetic field dependence of the electric polarization—are under intensive study, both theoretically [188–190] and experimentally [12, 114, 115, 191–194]. Therefore, the validity of the magnetoelectric sum rule in Eq. 3.18 can be checked by comparing these static magnetoelectric susceptibility data and the observed directional dichroism spectra. Based on symmetry analysis and the sum rule one can expect considerable directional dichroism in the low-frequency excitations of these magnetoelectric systems. Besides the good chances for directional effects, the study of the magnetic field dependence of the low-frequency magnetic excitations can provide an essential input for a theoretical model describing the magnetic properties of these materials. Most of the results of my magnetization and far-infrared optical studies, presented in this chapter, are published in Refs. [63, 64, 174, 195, 196].

4.1 Crystal and magnetic structure

The artificial Co-based multiferroic melilite crystals are isostructural with the natural occurring non-magnetic melilites first discovered in 1796 in Capo di
Figure 4.1: P\textsuperscript{2}1\textsubscript{1}m crystal structure of melilites. Co\textsuperscript{2+} ions are surrounded by oxygen tetrahedra (red), Ge/SiO\textsubscript{4} tetrahedra are orange, while Ba/Ca/Sr is denoted by blue sphere. Oxygen atoms at the corners of tetrahedra are omitted for clarity. (a) the tetragonal (001) plane of the crystal, (b) 3D image of the layered structure of the crystal viewed from the [001] direction. Rotational symmetries are indicated by blue lines along the axis of rotation, while projections of mirror planes onto the plane of the figure are shown by green lines. The axes of rotations and the normals of the mirror planes are also labeled by subscripts.

Bove, near Rome. [197] These compounds crystallize in the non-centrosymmetric tetragonal P\textsuperscript{2}1\textsubscript{1}m layered structure [198–201] where the layers are stacked along the tetragonal [001] axis, as shown in Fig. 4.1. In each layer Co\textsuperscript{2+} cations, surrounded by oxygen tetrahedra, form a square-lattice with the nearest neighbours connected along the [110] and [1\textup{T}0] directions of the crystal. The CoO\textsubscript{4} tetrahedra are bridged by Ge/SiO\textsubscript{4} tetrahedra, and these layers are separated by Ba/Ca/Sr\textsuperscript{2+} spacer ions. The two-fold screw axes of the P\textsuperscript{2}1\textsubscript{1}m space group are along the [100] and [010] directions, while the mirror planes correspond to the (110) and (1\textup{T}0) planes of the crystal.

In the tetrahedral crystal field of the oxygen ligands, the outermost 3d
orbits of the Co\(^{2+}\) ion split into the low-lying \(e\) subset consisting of \(d_{x^2-y^2}\) and \(d_{z^2}\) orbitals and the higher-energy \(t_2\) subset of \(d_{xy}, d_{xz}\) and \(d_{yz}\). The seven valence electrons of Co\(^{2+}\) fill the \(e\) orbitals and half-fill the three \(t_2\) orbitals, resulting in \(S = 3/2\) spin and a quenched orbital moment. However, since the CoO\(_4\) tetrahedra are flattened along the tetragonal [001] direction, the local symmetry felt by the Co\(^{2+}\) ion is further lowered to \(\bar{I}2m\). This leads to an axial magnetic anisotropy, i.e. a lower-energy level for \(S^z = \pm 1/2\) than for \(S^z = \pm 3/2\) states (in case of an elongated tetrahedron the situation would be the opposite). [202] Thus, at low temperatures and small magnetic fields the magnetic system of Co-based melilites can be modelled by an effective \(S = 1\) model. [196]

At low temperatures, below \(T_N \approx 5 - 8\) K, Co-spins order antiferromagnetically. The onset of the magnetic order in Ca\(_2\)CoSi\(_2\)O\(_7\) can be observed

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**Figure 4.2:** Temperature dependence of the magnetization of Ca\(_2\)CoSi\(_2\)O\(_7\) in \(\mu_0 H = 0.5\) T magnetic field, applied along the three main crystallographic directions ([100]: blue, [110]: green, [001]: red). Gray line shows the Curie-Weiss fit of the [100] data in the paramagnetic region, between 30 K and 300 K, corresponding to \(\Theta_{\text{CW}} = -12.3\) K Curie-Weiss temperature and a \(\mu_{\text{eff}} = 4.6 \mu_B\) effective magnetic moment. The inset focuses on the antiferromagnetic transition.
as a kink in the magnetization at $T_N \approx 5.7$ K in the inset of Fig. 4.2. Due to the strong single-ion anisotropy, the two-sublattice antiferromagnetic state has an easy-plane character with spins lying within the tetragonal (001) plane for all the three compounds. [191, 194, 200, 203, 204] The example of Ca$_2$CoSi$_2$O$_7$ in Fig. 4.2 clearly supports this concept, because the magnetization perpendicular to [001] exceeds the magnetization along [001] by about $\sim 30\%$. This difference is even larger in the sister compounds—$\sim 100\%$ in Ba$_2$CoGe$_2$O$_7$ [203] and $\sim 140\%$ in Sr$_2$CoSi$_2$O$_7$ [205]—and persists in the paramagnetic phase as well, [203, 206] indicating the single-ion nature of the anisotropy. In the ordered phase, in $\mu_0H = 0.5$ T magnetic field there is also a noticeable anisotropy within the (001) plane, i.e. the magnetization is larger along [100] than along [110]. This weak inplane anisotropy, also observed in Ba$_2$CoGe$_2$O$_7$ [195], disappears in the paramagnetic phase, and is explained by the multiferroic coupling between the polarization of neighbouring Co sites, [207] preferring magnetic moments lying along [110]. On the other hand, in Ba$_2$CoGe$_2$O$_7$ moderate fields of $\leq 1 - 2$ T applied in the tetragonal plane can already freely rotate the magnetization and the perpendicular staggered moments, indicating the weakness of the in-plane anisotropy. [12, 195] In zero field a small canting of $\sim 0.1^\circ$ develops. [192, 195] The corresponding, small a spontaneous ferromagnetic moment in Ba$_2$CoGe$_2$O$_7$ originates from a weak Dzyaloshinskii-Moriya interaction.

In the mean-field approximation, the temperature dependence of the paramagnetic susceptibility can be described by the Curie-Weiss law:

$$\chi^{mm}(T) = \frac{C}{T - \Theta_{CW}} + \chi_0, \quad (4.1)$$

where $C$ is the Curie-constant, proportional to the square of the $\mu_{eff} = g_{eff} \sqrt{J(J+1)}$ effective magnetic moment of the paramagnetic ion. $|\Theta_{CW}|$ gives the mean-field estimate of the ordering temperature, which is antiferromagnetic in case of $\Theta_{CW} < 0$ and ferromagnetic if $\Theta_{CW} > 0$, respectively. The $\chi_0$ term is responsible for the description of a temperature-independent paramagnetic contribution to the susceptibility.

In Fig. 4.2, the magnetization of Ca$_2$CoSi$_2$O$_7$ for magnetic fields in the (001)-plane was fitted by Eq. 4.1 in the 30 K – 300 K temperature range, resulting in a Curie-Weiss temperature of $\Theta_{CW} = -12.3$ K and $\mu_{eff} = 4.6\mu_B$, while $\chi_0$ was found negligible ($\mu_B$ stands for the Bohr-magneton). The sign and the magnitude of $\Theta_{CW}$ is in agreement with the onset of the antiferromagnetic ordering at $T_N \approx 5.7$ K. However, the fact that $|\Theta_{CW}|$ exceeds $T_N$ by a factor of more than two implies that either the magnetic order is low-dimensional or the magnetic interactions are frustrated. Indeed, in
Figure 4.3: Magnetic field dependence of the magnetization in the antiferromagnetically ordered phases of Ba$_2$CoGe$_2$O$_7$ and Ca$_2$CoSi$_2$O$_7$ displayed in panels (a) and (b), respectively, along the three main crystallographic directions, [100]: blue, [110]: green, [001]: red. The experiments were done using a vibrating sample magnetometer combined with a resistive 33 T magnet. The inset of panel (b) focuses on the magnetic anisotropy of Ca$_2$CoSi$_2$O$_7$ in the low-field region. Cyan ([100]), olive ([110]) and orange ([001]) dots indicate the results of low-field, low-noise measurements on a superconducting quantum interference device (SQUID) magnetometer at $T = 2$ K.

Ca$_2$CoSi$_2$O$_7$, Co sites in the neighbouring (001) layers are weakly coupled with respect to neighbouring Co ions within a single layer, resulting in quasi-2D magnetism. The effective magnetic moment corresponds to an effective g-factor of $g_{eff}^{\perp} = 2.38$ in the (001) plane, indicating an incomplete quench of the orbital moment and a significant role of the spin-orbit coupling. Similar values of effective inplane g-factors, $g_{eff}^{\perp} = 2.2, 2.3$ and 2.6 were found in the isostructural Ba$_2$CoSi$_2$O$_7$ [208], Sr$_2$CoGe$_2$O$_7$ [209] and Ba$_2$CoGe$_2$O$_7$ [195], respectively.

The magnetic field dependence of the magnetization is shown in Fig. 4.3 for Ba$_2$CoGe$_2$O$_7$ and Ca$_2$CoSi$_2$O$_7$. The case of Ba$_2$CoGe$_2$O$_7$ is more straightforward to interpret. As a consequence of the single-ion anisotropy, the magnetization gets saturated at different magnetic field values, $H_{Sat}^{\perp}$ and $H_{Sat}^{z}$, when the field is applied within the easy plane and along the hard axis, respectively. Prior to saturation, the magnetization follows a nearly linear field dependence due to the increasing canting of the sublattice moments for any
direction of the magnetic field. For the [001] direction, saturation is at higher fields than my measurement window, the necessary field is estimated to be $\mu_0 H_{Sat}^{z} \approx 36$ T [195] and experimentally found at $\mu_0 H_{Sat}^{z} = 37$ T [210]. Neither the $\mu_0 H_{Sat}^{z} \approx 16$ T saturation field, nor the slope of the magnetization shows considerable anisotropy within the tetragonal plane. The saturation magnetization, observed only for the in-plane directions in the magnetic field range of the measurement, is $\mu_{Sat} \approx 3.3 \mu_B$, corresponding to an effective g-factor of 2.2. The field dependence of the magnetization in Sr$_2$CoSi$_2$O$_7$ shows identical behavior to that of Ba$_2$CoGe$_2$O$_7$, and $\mu_0 H_{Sat}^{z} \approx 36$ T value was observed for Sr$_2$CoSi$_2$O$_7$ in pulsed magnetic field magnetization experiments. [205]

In case of Ca$_2$CoSi$_2$O$_7$ the situation is more complicated. Although the magnetization along [100] and [110] directions saturates to the same $\mu_{Sat} \approx 3.3 \mu_B$ value, there is an anisotropy in the (001) plane, which persists up to the saturation. While the magnetization along [100] is analogous to the one of Ba$_2$CoGe$_2$O$_7$, the susceptibility along [110] is smaller than along [100] in low fields and shows a steep jump at 11 T. The magnetization along [001] behaves in an even stranger way, presenting a plateau of $\mu_{plateau} \approx 2.65 \mu_B \approx 0.8 \mu_{Sat}$ in the field range of my experiments. The saturation along [001] is reached only in magnetic fields as high as $\mu_0 H_{Sat}^{z} \approx 60$ T [206] by a step-like increase.

In the low-field susceptibility of Ca$_2$CoSi$_2$O$_7$ a small anisotropy is observed [206] between the [100] and [010] directions, which should be equivalent in the P421m structure, hence, the true non-magnetic space group of Ca$_2$CoSi$_2$O$_7$ is P2$_1$2$_1$2$_1$, as it was also found in X-ray diffraction [198]. However, the deviation from the ideal tetragonal structure is minor, thus in the following I will assume tetragonal symmetry for Ca$_2$CoSi$_2$O$_7$ as well.

### 4.2 Static magnetoelastic properties

The multiferroic character of the static magnetoelastic properties of Co-based melilites has been intensively studied both theoretically, [188–190] and experimentally [12, 114, 115, 191–194]. Qualitatively, they show the same magnetoelastic behavior, hence I will describe the magnetoelastic properties of the most studied compound of this family, Ba$_2$CoGe$_2$O$_7$.

Without external magnetic field Ba$_2$CoGe$_2$O$_7$ has a non-chiral, non-polar but non-centrosymmetric structure with $\bar{T}_{[001]}2_{[100]}m_{[110]}$ point symmetry. When magnetic field is applied along one of the equivalent [110] or [110] axes, the symmetry reduces to the polar $2'_{[001]}m_{[110]}m'_{[110]}(2'_{[001]}m'_{[110]}m_{[110]})$ point group allowing ferroelectric polarization along the [001] crystal axis.
Figure 4.4: Magnetoelectric polarization of $\text{Ba}_2\text{CoGe}_2\text{O}_7$ in its antiferromagnetic phase. (a) Temperature dependence of the polarization component parallel to [001] in $\mu_0H = 5$ T magnetic field applied along various axes of the crystal. (b) Magnetic field dependence of the polarization parallel to [001] in magnetic field applied along [110]. Blue, green and orange colors correspond to different temperatures, while the black line is calculated based on the spin-dependent $p-d$ hybridization model. The inset shows the cobalt-oxygen tetrahedron together with the arrow indicating the direction of the magnetic moment on the Co site. Both figures are reproduced from Ref. [12].

This field-induced polarization was indeed observed, as reproduced in Fig. 4.4(a) from Ref. [12]. In finite magnetic fields the polarization appears upon $T_N$ and grows with decreasing temperature. When rotating the external field from [110] to [1T0] the sign of the polarization is reversed. If the field is applied along [100] or [001], no polarization is found, corresponding to the non-polar but chiral $2_{[100]}2'_{[010]}2''_{[001]}$ and $2'_{[100]}2'_{[010]}2''_{[001]}$ magnetic point groups, respectively.

The magnetic field dependence of the polarization in Fig. 4.4(b) shows a peculiar behavior, namely at $T = 2$ K first it grows steeply with the magnetic field and after a broad maximum at $\mu_0H_{\text{max}}^{110} \approx 7$ T it changes sign in fields above $\mu_0H_{\text{switch}}^{110} \approx 14$ T. At $T = 4$ K and $T = 6$ K both the magnitude of the polarization and the characteristic $H_{110}^{\text{max}}$, $H_{110}^{\text{switch}}$ fields are reduced with increasing temperature.

The observed magnetoelectric behavior of $\text{Ba}_2\text{CoGe}_2\text{O}_7$ can be explained by the spin-dependent $p-d$ hybridization model. [211] In Co-based melilites, the hybridization of the Co$^{2+}$ $3d$ orbitals with the $2p$ orbitals of the sur-
Figure 4.5: Magnetoelectric polarization component parallel to [001] measured in perpendicular magnetic field for Ba$_2$CoGe$_2$O$_7$. Panel (f): Polarization as a function of the polar angle of the magnetic field, $\phi_H$. $\phi_H$ is defined in panel (d). Panel (a), (b) and (c) show the cobalt magnetic moments in magnetic fields applied along [1\overline{1}0], [100] and [110] directions, which correspond to $\phi_H = -45^\circ$, $\phi_H = 0^\circ$ and $\phi_H = 45^\circ$, respectively. Panel (e): magnetization measured along the direction of the rotating magnetic field. All panels are reproduced from Ref. [12].

rounding oxygen atoms depends on the direction of the Co magnetic moment. [12, 193] Four oxygens form a tetrahedral cage around a cobalt ion as, seen in the inset of Fig. 4.4(b), and the emergent onsite polarization can be described [12] as

$$P \sim \sum_{i=1}^{4} (Se_i)^2 e_i,$$

(4.2)

where the sum corresponds to the contributions from each of the four Co-O bonds and $e_i$ denotes the unit vectors pointing from the cobalt towards each oxygen. Basically, the more parallel the Co moment is to a given bond, the stronger the bond gets. Correspondingly the Co$^{2+}$ moves towards a specific oxygen, inducing a local electric polarization. According to Eq. 4.2, the sign of $S$ does not influence the polarization, as expected due to the time reversal invariance of $P$. If the magnetic moment is parallel to the upper edge of the oxygen tetrahedron, the upper O$_1$ and O$_2$ oxygens attract the Co$^{2+}$ more than the lower ones, thus, a positive vertical polarization develops.
When the moment is rotated by $90^\circ$ to be parallel to the lower edge of the tetrahedron, the sign of the vertical polarization is reversed. If the magnetic moment is in the intermediate position, rotated by $45^\circ$ from the upper edge of the tetrahedron, the effect of the upper and lower pairs of oxygens cancels out and the polarization vanishes. In the unit cell of the melilite structure there are two CoO$_4$ tetrahedra, rotated by $48^\circ$ with respect to each other around the [001] axis of the crystal. [212] These two tetrahedra correspond to the two sublattices of the antiferromagnetic structure, thus, based on the magnetic structure, Eq. 4.2 can be straightforwardly applied to describe the magnetoelectric properties of the crystal.

Eq. 4.2 was systematically verified by rotating the magnetic field with fixed magnitude in the [001] plane of the crystal, while the polarization along [001] was measured as a function of the angle spaned by the field and [100]. [12] The spin-dependent $p-d$ hybridization model predicts a sinusoidal angular dependence of the polarization with $\pi$ periodicity, which was indeed observed in Ref. [12] as it is shown in Fig. 4.5.

In moderate magnetic fields, when the magnetization is a linear function of the applied field, the direction of the sublattice magnetizations can be straightforwardly expressed as a function of the orientation and the magnitude of the magnetic field. Then, the components of the magnetically induced ferroelectric polarization are directly determined from the orientation of the sublattice magnetizations within the spin-dependent hybridization model: [12, 211]

\[
P_{[001]} = A_p \left[ h_p \sin \theta - \sqrt{1 - (h_p \sin \theta)^2} \right] \sqrt{1 - (h_c \cos \theta)^2} h_c \cdot \\
\cdot \cos \theta \sin \phi,
\]
\[
P_{[010]} = A_p \left[ h_p \sin \theta - \sqrt{1 - (h_p \sin \theta)^2} \right] \sqrt{1 - (h_c \cos \theta)^2} h_c \cdot \\
\cdot \cos \theta \cos \phi,
\]
\[
P_{[001]} = A_c \left[ (h_p \sin \theta)^2 - h_p \sin \theta \sqrt{1 - (h_p \sin \theta)^2} - \frac{1}{2} \right] \left[ 1 - (h_c \cos \theta)^2 \right] \cdot \\
\cdot \sin(2\phi).
\]

Here $h_p = H/H_{Sat}^{\perp}$ and $h_c = H/H_{Sat}^z$ are the magnitude of the applied field $(H)$ in the units of the saturation fields. The $\theta$ and $\phi$ denote the azimuthal and polar angles of the magnetic field relative to the [001] and [100] axes, respectively. $A_c$ and $A_p$ are coefficients describing the strength of the magnetoelectric coupling for polarization along and perpendicular to the [001] axis. To make the formulae more compact, the tilting angle of the two inequivalent oxygen tetrahedra in the unit cell was approximated by $\pi/4$, which
Figure 4.6: Comparison of the static and optical ME properties of Ba$_2$CoGe$_2$O$_7$ (BCGO) based on the ME sum rule in Eq. 3.18. Dependence of the polarization ($P$) on the magnitude (a) and direction (d) of the magnetic field ($H$) applied along [110] and in the (110) plane, respectively. Solid/dashed line corresponds to experimental results [12]/calculations using Eqs. 4.3, 4.4 and 4.5. The slopes of the green lines are proportional to the corresponding elements of the ME tensor. Arrows labeled with $E$ and $H$ show the electric and magnetic components of the absorbed light in the corresponding optical experiment. These polarized absorption spectra, measured in Voigt configuration (light propagation perpendicular to the applied magnetic field), are presented in (b) and (e), in connection to the static results in (a) and (d), respectively. Red/blue lines indicate wave propagation along/opposite to [110]. The spectra are shifted vertically in proportion to $H$. The field dependence of static ME susceptibilities resulted from optical (squares) and static (solid line) experiments and first principle calculations [188] (dashed line) is shown in (c) and (f). The points corresponding to the slope of the green lines in the left panels are indicated by green dots. Static experiments, optical measurements and model calculations were carried out at $T = 2$ K, $T = 4$ K and $T = 0$ K, respectively. The figure is reproduced from my work, Ref. [174].
Figure 4.7: Comparison of the static and optical ME properties of Ba$_2$CoGe$_2$O$_7$ (BCGO), Ca$_2$CoSi$_2$O$_7$ (CCSO) and Sr$_2$CoSi$_2$O$_7$ (SCSO) based on the ME sum rule in Eq. 3.18. Dependence of the polarization ($P$) of BCGO on the direction of the magnetic field ($H$) rotated in the (001) (a) and (100) (d) planes, respectively. Solid/dashed line corresponds to experimental results [12]/calculations using Eqs. 4.3 and 4.5. The slopes of the green lines are proportional to the corresponding elements of the ME tensor. Arrows labeled with $E^\omega$ and $H^\omega$ show the electric and magnetic components of the absorbed light in the corresponding optical experiment. These polarized absorption experiments, carried out in the Faraday configuration (light propagation parallel or antiparallel to the applied magnetic field), are presented in (b)/(e), in connection to the static results in (a)/(d). Red/blue lines indicate wave propagation along/opposite to the magnetic field in BCGO, while wine/olive lines mean the same for CCSO. The spectra are shifted vertically in proportion to $H$. The absorption coefficient of CCSO is multiplied by a factor of two for better visibility. The field dependence of static ME susceptibilities resulted from optical (sybomles) and static experiments (solid, dashed and dotted line for BCGO, CCSO and SCSO, respectively) is shown in (c) and (f). The points corresponding to the slope of the green lines in the left panels are indicated by green dots. Static experiments, optical measurements and model calculations were carried out at $T = 2$ K, $T = 4$ K and $T = 0$ K, respectively. The figure is reproduced from my work, Ref. [174].
is close to the experimental value of 48° found for Ca$_2$Si$_2$O$_7$. [212] For Ba$_2$CoGe$_2$O$_7$, the saturation fields are $\mu_0 H_{Sat}^x \approx 16$ T and $\mu_0 H_{Sat}^y \approx 37$ T. By fitting the field dependence of the static polarization reproduced from Ref. [12] in Figs. 4.6(a), 4.7(a) and 4.7(d), I obtained $A_c = 180 \mu C/m^2$ and $A_p = 410 \mu C/m^2$ for Ba$_2$CoGe$_2$O$_7$. Using these parameters, the field dependence of every component of the static $\chi_{em}^{\delta\gamma c} = \partial P_\delta / \partial H_\gamma$ magnetoelectric tensor can be calculated for Ba$_2$CoGe$_2$O$_7$ according to Eqs. 4.3-4.5.

Another peculiar feature in the magnetoelectric behavior of the Co-based melilites is the jump-like sign-change of the electric polarization, for magnetic field slightly canted away from the [001] direction to the $\pm [110]$ or $\mp [010]$ directions. [12] These two cases are presented in Fig. 4.6 (d) and Fig. 4.7 (d), respectively. In $\mathbf{H} \parallel [001]$ the polarization vanishes corresponding to the $2'_{[100]}2'_{[010]}2_{[001]}$ magnetic point group. A small additional $\pm \mathbf{H} \parallel [010]$ field component breaks the $2'_{[010]}$ and $2_{[001]}$ symmetries, lowering the point group to $2'_{[100]}$ which allows electric polarization along the [100] axis. The systems corresponding to $\pm \delta H$ values are connected by the $2'_{[001]}$ rotation, hence, they should have polarization of opposite sign along [100]. The sign-change of the electric polarization around $\mathbf{H} \parallel [001]$ is also reproduced by the spin-dependent $p - d$ hybridization model in Eq. 4.3.

4.3 Dynamic magnetoelectric effect

As presented in Chapter 2, magnetoelectric multiferroics can differentiate between counter-propagating light beams. Based on the magnetoelectric sum rule in Eq. 3.18, this effect is expected to manifest mainly in the direction dependent absorption—directional dichroism—of the low-frequency magnetoelectric spin excitations of these materials. In this section, I will discuss the realization of directional dichroism in Co-based melilites.

4.3.1 Optical magnetoelectric effect

Ba$_2$CoGe$_2$O$_7$ was the first material studied in the THz frequency range exhibiting considerable directional dichroism. [46] In magnetic fields applied along [110], the magnetic symmetry is lowered to $2'_{[001]}m_{[110]}m_{[1\overline{1}0]}$ and electric polarization develops along [001]. For light propagation along [1T0], perpendicular to both the magnetization and the polarization, the absorption at the magnetoelectric spin-wave resonances is different for counter-propagating beams, realizing the optical magnetoelectric effect (OME). In Ref. [46] significant OME was found for the light polarization $\mathbf{E}^+ \parallel \mathbf{P}$, $\mathbf{H}^- \parallel \mathbf{M}$, while for the perpendicular polarization state of light no OME was observed.
rotating the crystal around the wave propagation axis, i.e. flipping the electric polarization while keeping the magnetization fixed, the sign of the directional absorption difference was reversed. Also, when the magnetization was reversed by the external magnetic field keeping the electric polarization intact, the sign of the OME was reversed. Hence, the absorption depends on the wave propagation direction with respect to the cross product of the electric polarization and the magnetization, i.e. the toroidal moment.\footnote{46}

I have extended the experiments of Ref.\footnote{46} to higher magnetic fields and lower frequencies as shown in Fig. 4.6(b) and (e). Red and blue absorption spectra correspond to wave propagation along and opposite to $\mathbf{T} = \mathbf{P} \times \mathbf{M} \parallel [T10]$, respectively. Besides the $\mathbf{E}_\omega \parallel \mathbf{P}$, $\mathbf{H}_\omega \parallel \mathbf{M}$ case in Fig. 4.6(b), I have observed a weaker OME in the perpendicular polarization in panel (e) as well. This effect only appears above the magnetic field range covered in Ref.\footnote{46}.

### 4.3.2 Magneto-Chiral Dichroism

Application of external magnetic field along the [100] or [010] directions breaks the mirror-plane symmetries of the system, and the magnetic point group is lowered to $2_1[100]2'_1[010]2'_1[001]$ and $2_2[100]2'_2[010]2'_2[001]$, respectively. This means that in melilites chirality can be induced by the magnetic field. This chirality, coming from the specific arrangement of the magnetic moments on the non-centrosymmetric lattice, is substantially different from the well known chirality of molecules, which is a consequence of the arrangement of static charges. Since the chirality in molecules is of non-magnetic origin and it is entirely determined by the arrangement of atoms, the handedness of the material cannot be changed. In contrast, by applying magnetic field along [010] instead of [100] the handedness of melilites can be switched, since the two cases are connected by the $m_{[110]}$ mirror plane. In other words, the mirror plane reflections connect the different electric current flows associated with the two magnetic configurations.

I have studied the low-frequency light absorption of $\text{Ba}_2\text{CoGe}_2\text{O}_7$ and $\text{Ca}_2\text{CoSi}_2\text{O}_7$ in their antiferromagnetic phase for light propagation parallel to the external magnetic field (Faraday geometry). The results of the $\mathbf{H} \parallel [100]$ and $\mathbf{H} \parallel [010]$ experiments for the two perpendicular linear polarization states of light are presented in Figs. 4.7(b) and (e). At a given frequency these materials are characterized by four different absorption coefficients corresponding to the possible combinations of the two $\pm k$ propagation directions and two orthogonal polarization states of light. In analogy with the conventional linear dichroism—absorption difference between beams with orthogonal linear polarizations—this novel phenomenon is termed as magneto-optical quadrochroism. Quadrochroism is realized for almost all excitation
Figure 4.8: Magnetic field dependence of the magneto-chiral dichroism in the low-frequency spin-wave excitations of Ba$_2$CoGe$_2$O$_7$ and Ca$_2$CoSi$_2$O$_7$. In all panels wave propagation is parallel (red) or antiparallel (blue) to the external magnetic field (Faraday geometry) and the polarization of light points along the $[001]$ axis. Absorption spectra are shifted in proportion to the field, spectra of Ba$_2$CoGe$_2$O$_7$ in (c) are two-times magnified compared to spectra of Ca$_2$CoSi$_2$O$_7$ in panels (a) and (b). Dashed lines show results of experiments with samples rotated by $\pi/2$ around the $[001]$ axis. In panels (a) and (c), the magnetic field is along $[010]$, corresponding to left-handed chirality, while in (b) the field is along $[010]$ leading to the right-handed chiral state. The figure is reproduced from my work, Ref. [64]

modes of Ba$_2$CoGe$_2$O$_7$ and Ca$_2$CoSi$_2$O$_7$ in Figs. 4.7(b) and (e).

To show that the quadrochroism is indeed of magneto-chiral origin, I performed the optical experiments for both $\mathbf{k} \parallel \mathbf{H} \parallel [100]$ and $\mathbf{k} \parallel \mathbf{H} \parallel [010]$ geometries, which are the mirror images of each other, thus, in case of magneto-chiral dichroism the more and the less absorbing directions should be interchanged with respect to the magnetic field. Indeed, the observed absorption spectra of Ca$_2$CoSi$_2$O$_7$ in Figs. 4.8(a) and (b) support my hypothesis about the magneto-chiral origin of the quadrochroism.

Another fact that further strengthens the magneto-chiral nature of the quadrochroism is the lack of any difference of absorption coefficients in case of magnetic fields and wave propagation along the $[110]$ axis of Ca$_2$CoSi$_2$O$_7$, as shown in Figs. 4.9(c) and (d). The $2m'_{[110]}m'_{[110]}$ magnetic point group, corresponding to the external field along $[110]$, is non-chiral, in agreement
Figure 4.9: Magnetic field dependence of the low-frequency spin-wave excitations of Ca$_2$CoSi$_2$O$_7$ in magnetic fields within the (001) tetragonal plane. In all panels wave propagation is parallel (red) or antiparallel (blue) to the external magnetic field (Faraday geometry) and the polarization of light is indicated in the legends. Absorption spectra are shifted in proportion to the applied magnetic field. In panels (a) and (b) magnetic fields are along $\mathbf{r}_{100}$, inducing left-handed chirality in the material, while in (c) and (d) fields are along $\mathbf{r}_{110}$ leading to non-chiral, but polar state.

with the lack of magneto-chiral dichroism in this configuration.

4.4 Kramers-Kronig analysis of the magnetolectric susceptibility

For the Co-based melilites, several elements of the static ME tensor can be directly determined from the measured field dependence of the ferroelectric polarization reported in the literature. \cite{12, 114, 115, 191-194} In those cases when experimental curves are not available, the ME tensor elements can be evaluated using the spin-dependent $p-d$ hybridization model according to Eqs. 4.3, 4.4 and 4.5.

Fig. 4.6(a) displays the ferroelectric polarization induced along the [001]
axis in Ba$_2$CoGe$_2$O$_7$ by magnetic fields applied parallel to the [110] direction, $P_{[001]}(H_{[110]})$, as reproduced from Ref. [12]. The field dependence of the $\chi_{[001][110]}^m$ static ME tensor element for external fields along the [110] axis, given by the derivative $c\frac{\partial P_{[001]}}{\partial H_{[110]}}$, is shown in Fig. 4.6(c). Via the magnetoelectric sum rule in Eq. 3.18, this element of the static ME tensor is related to the integral of the directional dichroism spectrum in the Voigt configuration, where the magnetic component of light is parallel to the static magnetic field applied along the [110] direction and the electric component of light is parallel to the [001] axis. In this configuration, the directional dichroism spectra reported for Ba$_2$CoGe$_2$O$_7$ by Ref. [46] correspond to the difference of the red and blue curves in Fig. 4.6(b). The comparison between the static and optical data using Eq. 3.18 is shown in Fig. 4.6(c).

The following part of Fig. 4.6 and the Fig. 4.7 shows similar analysis for other three elements of the ME tensor in Ba$_2$CoGe$_2$O$_7$. In Fig. 4.7 data for Sr$_2$CoSi$_2$O$_7$ and Ca$_2$CoSi$_2$O$_7$ are also included. The dependence of the ferroelectric polarization on the orientation of a constant field $\mathbf{H}$ is shown in Fig. 4.6(d), Fig. 4.7(a) and (d). The directional dichroism spectra in these three cases are displayed in Fig. 4.6(e), Fig. 4.7(b) and (e), while the comparison between the static and optical data is given in Figs. 4.6(f), 4.7(c) and (f), respectively.

The $P_{[100]}(\theta)$ curve in Fig. 4.7(d), where $\theta$ is the angle of the magnetic field relative to the [001] axis, is reproduced from Ref. [12]. Since the tilting of the magnetic field from the [010] direction by a small angle of $\delta\theta$ introduces a weak transversal field $\delta\mathbf{H} = (0, 0, H \sin \delta \theta)$, for $\mathbf{H} \parallel [010]$ one obtains

$$\chi_{[100][001]}^m \left( H_{[010]} = H \right) = c \left. \frac{\partial P_{[100]}}{\partial H_{[001]}} \right|_{H_{[010]}=H} \approx \left. \frac{c}{H} \frac{\partial P_{[100]}}{\partial \theta} \right|_{H_{[010]}=H} \approx \lim_{\delta \to 0+} \frac{2c}{\pi H} P_{[100]} \left( H_{[0\bar{1}]} = H \right), \quad (4.6)$$

where $\lim_{\delta \to 0+} P_{[100]} \left( H_{[0\bar{1}]} = H \right)$ is the amplitude of the $P_{[100]}(\theta)$ function. The corresponding optical experiment can be realized in the Faraday configuration, where $\mathbf{H} \parallel [010]$, while the electric and magnetic components of light are parallel to the [100] and [001] axes, respectively. These THz absorption spectra are shown for the two opposite wave propagation directions in Fig. 4.7(e).

The $P_{[001]}(\phi)$ curve in Fig. 4.7(a) is taken from Ref. [12] and the $P_{[110]}(\theta)$ curve in Fig. 4.7(d) is calculated using Eqs. 4.3-4.5. In the former and later cases, the elements of the static ME tensor are respectively obtained
according to

\[ \chi_{[001][010]}^\text{em} (H_{[100]} = H) = c \frac{\partial P_{[001]}}{\partial H_{[010]}} \bigg|_{H_{[100]}=H} \approx \frac{c}{\mathcal{H}} \frac{\partial P_{[001]}}{\partial \phi} \bigg|_{H_{[100]}=H} \approx \frac{2c}{\mathcal{H}} P_{[001]} (H_{[110]} = H) \]  

(4.7)

for \( \mathbf{H} \parallel [100] \), where \( P_{[001]} (H_{[110]} = H) \) is the amplitude of \( P_{[001]} (\phi) \), and according to

\[ \chi_{[110][001]}^\text{em} (H_{[110]} = H) = c \frac{\partial P_{[110]}}{\partial H_{[001]}} \bigg|_{H_{[110]}=H} \approx \frac{c}{\mathcal{H}} \frac{\partial P_{[110]}}{\partial \theta} \bigg|_{H_{[110]}=H} \]  

(4.8)

for \( \mathbf{H} \parallel [110] \). The corresponding THz absorption spectra are shown in Fig. 4.7(b) and (e), respectively.

The comparison between the ME tensor elements calculated from the static and optical data presented in the last columns of Fig. 4.6 and 4.7 supports the applicability of the ME sum rule in the Co-based melilites. The magnitude and the field dependence of the static and optical data in Fig. 4.6(f), 4.7(c) and (f) show quantitative agreement. Their difference can be attributed to the following factors:

- the directional dichroism measurements were performed at \( T = 4 \) K, while the static experiments were carried out at \( T \leq 2 \) K where the ME coefficients are larger by \( \sim 10 \sim 20\% \),
- the two set of experiments were performed on samples from different growths,
- in Figs. 4.7(b) and (e) the initial linear polarization of light beams can change during the propagation through the samples due to natural and magnetic circular dichroism, hence, the directional dichroism does not exactly correspond to a single off-diagonal component of the magnetoelectric tensor
- the model used to calculate the field dependence of the static magnetoelectric coefficients is not accurate due to the linear field dependence of the magnetization assumed here to reduce the number of fitting parameters,
- uncertainty in the geometrical factors of samples used in the static and optical experiments may also cause an error of typically \( \sim 10 \sim 20\% \).
In the case of the spectra of Fig. 4.6(e), 4.7(b) and (e) the magnetic component of light is perpendicular to the static magnetic field which lies in the (001) easy plane. Corresponding to the small magnetic anisotropy within the easy plane, in these cases a resonance, which is nearly a Goldstone mode in zero field, is excited with a frequency approximately proportional to the external field. The zero field frequency of the mode corresponds to the geometrical mean of the easy-plane anisotropy and the antiferromagnetic exchange and it is less than 75 GHz. Consequently, its frequency remains considerably smaller than those of the other magnon modes. Thus, the dominant contribution to the sum rule in the Eq. 3.18 comes from this mode due to the \(\omega^2\) frequency denominator. This mode reaches my frequency window only in fields higher than 6 T, hence optical data are shown only above this field in Figs. 4.6(f), 4.7(c) and (f).

Usually this mode is not allowed in an easy-plane magnet if the magnetic component of light is parallel to the static magnetic field as also discerned in Fig. 4.6(b). Correspondingly, in Fig. 4.6(c) the ME tensor element calculated from the directional dichroism data is smaller than those for the transverse spin excitations shown in Figs. 4.6(f), 4.7(c) and (f).

Moreover, the ME tensor element calculated from the sum rule in Fig. 4.6(c) is one order of magnitude smaller than the value determined from the static measurement, though they both change sign in the same field region of \(\mu_0 H = 7 \text{–} 9 \text{ T}\). This significant difference may come from directional dichroism exhibited by excitations out of the range of my optical detection. In a classical or an \(S = 1/2\) quantum mechanical spin system with a two-sublattice easy-plane antiferromagnetic ordering two magnon modes are expected: a Goldstone mode and an optical magnon mode, gapped by the geometrical mean of the antiferromagnetic exchange and the anisotropy between the easy plane and the hard axis. For materials with spins larger than \(S = 1/2\), additional modes can appear in the spin excitation spectrum (e.g. spin-stretching modes) if the magnetic anisotropy is strong and/or the inversion symmetry is broken. Indeed all the six modes expected theoretically for an \(S=3/2\) easy-plane antiferromagnet [196] are observed in the spectra measured on \(\text{Ba}_2\text{CoGe}_2\text{O}_7\). Therefore, to explain the difference in Fig. 4.6(c), one should consider that low-energy phonon modes may also contribute to the optical ME effect by their coupling to magnon modes. Though directional dichroism has not been directly observed for phonon modes so far, recent optical studies on multiferroic \(\text{Ba}_3\text{NbFe}_2\text{Si}_2\text{O}_{14}\) reported about the magnetoelectric nature of low-energy lattice vibrations. [213] As another possibility, the low-frequency dynamics of ME domain walls could also contribute to the static ME susceptibility. However, the presence of such ME domain-wall dynamics should be restricted to the region of weak magnetic fields in \(\text{Ba}_2\text{CoGe}_2\text{O}_7\),
since the single-domain multiferroic state is realized in fields $\mu_0 H > 1\, \text{T}$ applied within the easy-plane. [12, 195]

### 4.5 Selection rules for magnetoelectric excitations

As presented in the previous sections, in the magnetoelectric Co-based melilite family the low-frequency spin excitations are coupled to local electric dipoles, thus, these resonances are not of exclusively magnetic character. Some collective spin modes in magnetoelectric multiferroics can even possess entirely electric dipole character, and are termed as electromagnons. [214] In fact, to achieve considerable directional dichroism at a given resonance, the magnitude of the transition matrix elements of the electric- and magnetic dipole operators should be of similar magnitudes for this transition. Thus, magnetoelectric multiferroics show peculiar selection rules even in the dipolar approximation.

To demonstrate the various possible selection rules in multiferroics, I performed a detailed analysis of the low-frequency optical resonances of $\text{Ba}_2\text{CoGe}_2\text{O}_7$ in magnetic fields $H \parallel [110]$. In this case the relevant high symmetry axes of the magnetic system are the direction of the magnetic field, $x \parallel [110]$, the direction of the induced static electric polarization, $z \parallel [001]$, and the direction of their cross product, termed hereafter as the toroidal moment, $y \parallel [1\bar{1}0]$. To determine the selection rules, I studied the optical absorption for various combinations of wave propagation and light polarization along these axes. Moreover, experiments were repeated in reversed magnetic fields to detect directional dichroism. Two sets of examples of the resulted spectra are presented in Figs. 4.6(b) and (e).

For magnetic field along $x$, the magnetic point group of the system is $2'_{z}m_{x}m'_{y}$, thus, natural circular dichroism or birefringence is not expected, which is usually present in chiral systems. However, when light propagates parallel to the magnetic field, magnetic circular dichroism and birefringence can occur due to the Faraday effect. In the analysis I neglected the deviation of the light polarization from the initial linear polarization and considered the anisotropy (linear birefringence and dichroism) along/perpendicular to the $z$ axis as the dominating anisotropy term resulting in approximately linear eigenstates of light polarized along/perpendicular to the $z$ axis. Thus, the $\hat{\varepsilon}$ electric permittivity and $\hat{\mu}$ magnetic permeability tensors are approximated by their diagonal elements, neglecting the small off-diagonal terms.

According to Eq. 3.11, in a given experimental geometry with $E^{-}$ along
Figure 4.10: Observed selection rules in Ba$_2$CoGe$_2$O$_7$ in external magnetic field along [110]. The colormaps in panels (a)-(c) and (d)-(f) show the field dependence of the terms in the absorption coefficient related to the magnetic dipole and electric dipole active character of the modes, respectively, where $x = [110]$, $y = [1\bar{1}0]$ and $z = [001]$ axes, respectively. The same scale is used for all panels. Measurements were carried out in 1 T field steps and the data were interpolated. Dots in the low-frequency low-field region in (b) and (c) resulted from electron spin resonance experiment and are not proportional to the absorption coefficient of the resonance.
the $\beta$ and $\mathbf{H}$ along the $\gamma$ Cartesian axis, the average of the absorption coefficients ($\pi$) observed for opposite propagation directions in the first approximation contains only the terms corresponding to the imaginary parts of $\varepsilon_{\beta\beta}$ and $\mu_{\gamma\gamma}$:

$$\pi(\omega) = \frac{2\omega}{c} \Im(\varepsilon) = \frac{2\omega}{c} \Im(\frac{\varepsilon(\omega)}{\varepsilon_{\beta\beta}}) \mu_{\gamma\gamma}(\omega)$$

$$\approx \frac{\omega}{c} \Im(\varepsilon_{\beta\beta}(\omega)) + \frac{\sqrt{\varepsilon_{\beta\beta}}}{c} \Im(\mu_{\gamma\gamma}(\omega)).$$

(4.9)

Here the first/second term stands for the absorption due to electric/magnetic dipole processes. The frequency independent real part of $\varepsilon_{\beta\beta}$ originates from electric excitations at higher frequencies—e.g. phonons—and is denoted by $\varepsilon_r^{\text{ee}}$, while the real part of $\mu$ is considered to be unity. Due to the tetragonal symmetry of the paramagnetic state $\varepsilon_\alpha^{\text{ex}} = \varepsilon_r^{\text{ee}} = \varepsilon_\alpha^{\text{ex}}$.

Thus, from the absorption spectra recorded at a given magnetic field but in different geometry one can separate the absorption contributions of the individual diagonal elements of $\hat{\varepsilon}$ and $\hat{\mu}$. For instance by subtracting spectra measured with the same polarization of the electric field of light but with different direction of the oscillating magnetic component, one gets the difference $\Im(\mu_{\beta\beta}(\omega)) - \Im(\mu_{\gamma\gamma}(\omega))$. In this difference spectrum the electric dipole processes fall out, positive/negative absorption peaks correspond to $\Im(\mu_{\beta\beta}(\omega))/\Im(\mu_{\gamma\gamma}(\omega))$, respectively. However, a careful cross-check is needed since resonances present in both $\Im(\mu_{\beta\beta}(\omega))$ and $\Im(\mu_{\gamma\gamma}(\omega))$ disappear as well. If absorption spectra are measured for all the six possible combinations of light polarization and wave propagation axis, the diagonal elements of $\hat{\varepsilon}$ and $\hat{\mu}$ can be unambiguously determined.

The results of this analysis is presented in Fig. 4.10. The intensity of the magnetic-dipole and electric-dipole processes is approximately the same, thus, the low-frequency excitations of Ba$_2$CoGe$_2$O$_7$ have strong magnetoelectric nature. In fact, all of the resonances are electric dipole active at least in one experimental configuration. The intensity maps corresponding to $\mu_{xx}$ and $\varepsilon_{yy}$ show the same resonances as do the maps for $\mu_{yy}$ and $\varepsilon_{xx}$, while the picture in case of $\mu_{zz}$ and $\varepsilon_{zz}$ is different.

These selection rules reflect the spatial part of the magnetic point symmetry group, $2_1 m_x m_y$. In this point group, the polar vector along $z$ belongs to the $A_1$, the axial vector along the $z$ axis—$R_z$—to $A_2$, while $x$ and $R_y$ to the $B_1$, and $y$ and $R_x$ to the $B_2$ irreducible representation. In a quantum-mechanical picture the operator corresponding to the electric dipole process behaves as a polar vector, while the magnetic dipole operator is an axial vector. Since $x$ and $R_y$ belong to the same $B_1$ irreducible representation,
\[ |\langle f | P_x | \hat{i} \rangle|^2 \text{ and } |\langle f | M_y | \hat{i} \rangle|^2 \] transition matrix elements contributing to \( \epsilon_{xx} \) and \( \mu_{yy} \) according to Eqs. 1.4 and 1.5, respectively, are non-zero for the same resonances (between the same \( i \) initial and \( f \) final energy eigenstates). Similarly, \( \mu_{xx} \) and \( \epsilon_{yy} \) are expected to have the same modes since both of their operators belong to \( B_2 \).

Beyond the presence or absence of a resonance mode in a given configuration one can get more detailed information from the colormap indicating the relative magnitude of the different transition matrix elements. In case of the mode with frequency proportional to the applied field, the magnitude of the transition matrix element is much weaker in \( \mu_{zz} \) than in \( \mu_{yy} \) for the same excitation, i.e., the same precession of the magnetization around the field. Due to the anisotropy of the magnetic system the precession becomes elliptical with its major axis along \( y \) and its minor axis along \( z \). According to Eq. 3.9, the low-frequency magnetic excitations dominate the static magnetic susceptibility, thus, it is indeed expected that this mode is characterized by larger transition matrix element when excited by magnetic fields oscillating within the easy plane, than along the hard axis.

### 4.6 Magnetic field dependence of the resonance frequencies

When investigating magnetically ordered materials, static measurements of the magnetic ground state, e.g. the study of the temperature and field dependence of the magnetic susceptibility in various geometries, give only limited information about the magnetic interactions governing the behavior of the material. Spectroscopic methods, on the other hand, offer a complementary tool by providing the energies of the excited states as a function of the relevant external parameters. In this section I am going to discuss the evolution of resonance frequencies of Co-based melilites in external magnetic field.

**Ba$_2$CoGe$_2$O$_7$**

Fig. 4.11 presents the observed low-frequency optical resonances of Ba$_2$CoGe$_2$O$_7$ in case of three inequivalent high symmetry directions of the magnetic field, \([001]\), \([100]\) and \([110]\). Only the excitations observed in the Faraday-configuration are shown since the Voigt-geometry measurements have not resulted in additional resonance modes. The lowest lying modes (below \( \omega \sim 0.6 \) THz) can be understood in the frame of a classical two sublattice mean-field model, while the appearance of higher frequency resonances indicate the need for a more sophisticated description of the magnetic system.
Figure 4.11: Observed magnetic field dependence of the optical resonance frequencies in Ba$_2$CoGe$_2$O$_7$. The external magnetic field and the wave propagation was parallel—Faraday-configuration—and both lied along [001], [100] and [110] axes in panels (a), (b) and (c), respectively. The polarization of light is indicated in the legends of the panels. The experiments were performed in the antiferromagnetic phase at $T = 2 - 3$ K. The results of a classical two-sublattice mean-field calculation, partly reproducing the observed resonance frequencies, is presented by gray lines.
In a classical description, based on the general mean-field theory of classical spin systems in Ref. [215], the magnetic system of Co-based melilites can be modelled by an anisotropic $S = 3/2$ model. Since the ground state of the Co$^{2+}$ ion sitting in a flattened tetrahedron is the $S^z = \pm 1/2$ Kramers-doublet [202], the easy plane magnetic anisotropy originating from the tetragonal $42m$ symmetry of the local crystal field of Co sites can be described in the energy of the spin system as $\Lambda(S^z)^2$ for each spin with positive $\Lambda$ coefficient. Considering the low symmetry of the system, an anisotropy of the antiferromagnetic exchange, $J^z \neq J^x$ is also introduced. The corresponding classical two-sublattice antiferromagnetic mean-field Hamiltonian can be written as

$$\mathcal{H} = 2J^\perp S_A^z S_B^z + 2J^z S_A^z S_B^z + \Lambda (S_A^z)^2 + (S_B^z)^2 - g\mu_B \mu_0 H (S_A + S_B),$$

(4.10)

where $S_{A/B}^{z/plane}$ denote the A/B sublattice moments lying along/perpendicular to the [001] axis. The last term stands for the Zeeman-energy. The model is isotropic within the (001) plane. The zero-field ground state is an antiferromagnetic order in the (001) plane, where the $I = S_A - S_B$ staggered magnetization breaks the rotational symmetry around [001]. The magnetic anisotropy is reflected in the diagonal components of the magnetic susceptibility,

$$\chi_{\perp mm} = g \frac{2J^\perp}{2J^\perp}$$

(4.11)

$$\chi_{zz mm} = g \frac{J^z}{J^\perp + J^z + \Lambda}.$$  

(4.12)

In case of Ba$_2$CoGe$_2$O$_7$ $\chi_{\perp mm}^{zz} \approx 2.1\chi_{zz mm}^{mm}$, as seen in Fig. 4.3, and the anisotropy does not disappear above $T_N$, [192] indicating the dominant role of $\Lambda$.

Without external magnetic field, one of the two resonances of the system described in Eq. 4.10 has zero frequency, corresponding to the free rotation of $I$ in the (001) plane. In magnetic field along [001] this mode remains gapless (acoustic mode), while for a field in the (001) plane it becomes gapped in proportion to the external field:

$$\omega_{ac}^\perp (H \perp [001]) = g\mu_B \mu_0 H \sqrt{J^\perp + J^z + \Lambda} = g\mu_B \mu_0 H \sqrt{\chi_{\perp mm}^{mm}}.$$  

(4.13)

The slope of this mode is renormalized by the ratio of the static susceptibilities as compared to the paramagnetic resonance of the free ion. This mode can be excited by oscillating fields perpendicular to the static magnetic field, thus it is visible in all of the Faraday-configuration experiments presented in Figs. 4.11(b) and (c).
The optical resonance is gapped due to the single ion anisotropy and the anisotropic nature of the exchange interaction, which can be described by a characteristic field. The field dependence of the resonance frequencies can be described by the characteristic fields $H_{EA}$ and

$$
\mu_B\mu_0 H_{EA} = \frac{4S}{g} \sqrt{J^\perp (J^\perp - J^z + \Lambda)}
$$

characteristic field. The field dependence of the resonance frequencies can be described by the characteristic fields $H_{EA}$ and

$$
\mu_B\mu_0 H_{Sat}^\perp = \frac{4S}{g} J^\perp,
$$

the latter being the in-plane saturation magnetic field. With these two parameters the frequency of the gapped mode for fields applied along and perpendicular to the $[001]$ axis, respectively:

$$
\omega_{opt}^z (H \parallel [001]) = g\mu_B\mu_0 H_{EA}\sqrt{1 + \left(\frac{H}{H_{EA}}\right)^2}
$$

$$
\omega_{opt}^\perp (H \perp [001]) = g\mu_B\mu_0 H_{EA}\sqrt{1 - \left(\frac{H}{H_{Sat}^\perp}\right)^2}.
$$

The $\omega_{opt}^z$ resonance mode is excited by oscillating fields perpendicular to the static magnetic field, while $\omega_{opt}^\perp$ only by parallel static and dynamic fields.

This model describes the field dependence of the lowest-frequency excitations of $\text{Ba}_2\text{CoGe}_2\text{O}_7$. Considering a $g = 2$ g-factor, corresponding to the lowest-energy $S^z = \pm 1/2$ states, the observed $\chi_{mm}/\chi_{zz} \approx 2.1$ ratio of the low-field static susceptibilities is reproduced from the $d\omega/dH$ slope of the acoustic mode in Fig.s 4.11(b) and (c). The curvature of $\omega_{opt}^\perp$ in Fig. 4.11(c) corresponds to a saturation field of $\mu_0 H_{Sat}^\perp = 14$ T, which is somewhat lower than that I have observed in the static magnetization experiments in Fig. 4.3(a). The zero-field gap of $\omega_{opt}^\perp$ sets the value of the exchange anisotropy to $\mu_0 H_{EA} = 19.35$ T. Using these parameters, the field dependence of the modes is reproduced as shown by gray lines in Fig. 4.11. The corresponding exchange constants in Eq. 4.10 are $J^\perp = 0.54$ meV, $J^z = 0.62$ meV and $\Lambda = 1.11$ meV. Although $J^z > J^\perp$, the dominating $\Lambda$ single-ion anisotropy forces the spins into the (001) plane in the ground state. To rotate an individual spin from the (001) plane to the [001] axis, in the classical model $\Delta E = (2J^\perp + \Lambda)S^2 \approx 4.9$ meV energy is needed, which roughly coincides with the frequency of the mode starting from 1 THz in zero field. Thus, one can speculate that this resonance, not covered by a classical mean-field model, corresponds to the excitation from the ground state $S^z = \pm 1/2$ Kramers-doublet [202] to the $S^z = \pm 3/2$ Kramers-doublet of the Co$^{2+}$ ion.
Indeed, in a generalized spin-wave theory [196], the resonances starting from $\omega(H = 0) \approx 1$ THz are identified as spin-stretching modes, corresponding to excitations generated by spin-quadrupolar or spin-nematic [207] operators. This unusual situation arises because of the significant single-ion anisotropy acting on the $S = 3/2$ moment. In this case, the spin cannot be considered as a classical vector, and has no definite length any more. In fact, if $\Lambda \gg J$, the $S^z = \pm 3/2$ subspace is missing from the ground state, reducing the effective length of the spin to $S = 1$. In terms of symmetry operations, Cartesian components of the electric polarization operator are equivalent to spin-quadrupolar operators, hence the spin-stretching modes can be viewed as magnetic footprints of the polarization dynamics. Thus, the unconventional spin-stretching modes are visible in the far-infrared spectroscopy via the magnetoelectric coupling.

The generalized spin-wave theory, taking into account the dynamics of the spin-quadrupolar moments, is able to reproduce all the major features of the observed optical spectra, as presented in Ref. [196]. The parameter set used for the calculation nearly corresponds to my classical parameters, the only difference is the use of anisotropic g-factor in Ref. [196] to quantitatively reproduce the magnetic field dependence of the resonances. However, the quantum-mechanical spin-wave theory results in six excitations—three for each of the Co sublattices, corresponding to the $S = 3/2$ spin—while in an external field along [110] (Fig. 4.11(c)) there are up to 10 resonances at a given magnetic field value, indicating a more complex magnetic structure.

**Ca$_2$CoSi$_2$O$_7$**

As demonstrated in the previous section, the field dependence of some of the spin-wave resonance frequencies in Ba$_2$CoGe$_2$O$_7$ can be interpreted even within a simple classical mean-field model, and the other, higher frequency modes are described by the quantum-mechanical theory of spin-stretching excitations. In contrast, I could not describe the low-frequency resonances of Ca$_2$CoSi$_2$O$_7$ in a classical way and no quantum-mechanical description is known either so far.

In magnetic field along the [001] axis, the absorption spectra of the two compounds are compared in Fig. 4.12. In zero field, the single absorption peak of Ca$_2$CoSi$_2$O$_7$ is about five times smaller than those of Ba$_2$CoGe$_2$O$_7$ and has significantly lower frequency, $\omega(H = 0) = 0.39$ THz. Due to the lower frequency and the approximately two times larger width of its resonance peak, Ca$_2$CoSi$_2$O$_7$ can have approximately the same static susceptibility for magnetic fields in the (001) plane as Ba$_2$CoGe$_2$O$_7$ according to Eq. 3.9 (The field dependent magnetization of the two compounds is presented in Fig. 55.
Figure 4.12: Magnetic field dependence of low-frequency spin-wave resonances in Ca$_2$CoSi$_2$O$_7$ (a) and Ba$_2$CoGe$_2$O$_7$ (b). The magnetic field was applied along the [001] axis, and the oscillating magnetic component of light was perpendicular to the static field. Spectra are vertically shifted relative to each other in proportion to the applied static magnetic field. The experiments were performed in the antiferromagnetic phase at $T = 2 - 3$ K. The scale of absorption is five times magnified in case of Ca$_2$CoSi$_2$O$_7$ in panel (a) as compared to panel (b).

4.3). The magnetic resonance of Ca$_2$CoSi$_2$O$_7$ first softens, then in magnetic fields above $7 - 8$ T hardens with increasing field along the [001] axis, and the absorption peak gets significantly broader.

When applying the magnetic field in the (001) plane, for fields along [110] a single resonance is visible which gets harder and gains oscillator strength with increasing magnetic field, as seen in Figs. 4.9(c) and (d). Besides this mode, for fields along [100] additional resonances are observed (Figs. 4.9(a) and (b)). In high magnetic fields, above the saturation, all the mode frequencies have a linear field dependence, as presented in Fig. 4.8(a). Interestingly, even after the saturation the excitation spectra of Ca$_2$CoSi$_2$O$_7$ and Ba$_2$CoGe$_2$O$_7$ (Fig. 4.8(c)) show different behavior. While in case of Ba$_2$CoGe$_2$O$_7$ the intensity of the excitations is roughly the same in the whole $\mu_0 H = 0 - 30$ T magnetic field range, the resonances of Ca$_2$CoSi$_2$O$_7$ gain intensity with increasing magnetic field. For Ba$_2$CoGe$_2$O$_7$ there are only two
resonances visible in the high fields, while Ca$_2$CoSi$_2$O$_7$ shows five resonances. This indicates the lower symmetry of Ca$_2$CoSi$_2$O$_7$, i.e. a larger magnetic unit cell in accordance to neutron scattering studies \cite{216}, with correspondingly more excitation modes.

## 4.7 Optical para-magnetolectric effect

For the first sight, applications based on multiferroic compounds seem to be limited to low temperatures where electric and magnetic order coexist in these materials. However, in the paramagnetic phase of Co-based melilites the magnetic symmetry in external magnetic field is the same as in the antiferromagnetic phase, thus the same magnetoelectric effects are expected to appear when the material is exposed to magnetic field at higher temperatures. Indeed, recent studies on melilites (Ca$_2$CoSi$_2$O$_7$ \cite{206}, Ba$_2$CoGe$_2$O$_7$ \cite{193} and Sr$_2$CoSi$_2$O$_7$ \cite{114, 115}) revealed that application of external magnetic field can recover the electric polarization via the para-magnetolectric effect even far above the material’s multiferroic ordering temperature, $T_N = 6 - 8$ K. Based on the symmetry analysis and the static magnetoelectric data one can also expect directional dichroism to emerge in the paramagnetic phase of melilites.

In non-centrosymmetric materials without spontaneous magnetic ordering, magnetoelectricity can appear via the para-magnetolectric effect. \cite{217} In a phenomenological description the para-magnetolectric polarization is a
bilinear function of the external magnetic field:

\[ P_i = \frac{1}{2} \sum_{j,k} \beta_{ijk} H_j H_k, \]  

(4.18)

where \( \beta_{ijk} \) is the para-magnetoelectric susceptibility tensor and \( i, j, k \) stand for Cartesian axes. The tensor is symmetric in its last two indices and most of the 27 elements of the tensor vanish in the \( \text{PT}_2 \text{I} \text{m} \) non-magnetic symmetry of melilites. In the \( a \parallel [100], b \parallel [010], c \parallel [001] \) basis, the twofold rotations around the \( a, b, c \) axes forbid tensor elements having two or three identical indices. The 4c symmetry requires the \( a \) and \( b \) indices to be interchangeable, thus leading to only two independent elements:

\[
\beta_{abc} = \beta_{acb} = \beta_{bca} \]  

(4.19)

\[
\beta_{cab} = \beta_{cba}. \]  

(4.20)

In the static magnetoelectric experiments shown in Fig. 4.13 the magnetic field points along the [110] axis, giving \( H_a = H_b = H/\sqrt{2} \), while the electric polarization was measured along the \( c \) axis:

\[ P_c (H \parallel [110]) = \frac{1}{2} (\beta_{cab} + \beta_{cba}) H^2 = \frac{1}{2} \beta_{cab} H^2. \]  

(4.21)

For instance, the quadratic \( P - H \) curve observed for \( \text{Ba}_2\text{CoGe}_2\text{O}_7 \) \cite{193} at \( T = 20 \text{ K} \approx 3T_N \) and shown in Fig. 4.13(b), corresponds to \( \beta_{cab} = 0.4 \text{ \mu Cm}^{-2}\text{T}^{-2}. \)

In the frame of the spin-dependent \( p - d \) hybridization model \cite{12} one can calculate the elements of the \( \hat{\beta} \) tensor using the phenomenological \( A_c \) and \( A_p \) magnetoelectric coupling constants determined from the low temperature static magnetoelectric data in Section 4.2. In the paramagnetic phase the ordered moments are parallel to the magnetic field and their lengths, \( M \), depend on the temperature via the \( \chi^{mm}(T) \) magnetic susceptibility: \( M(H, T) = \chi^{mm}(T)H \). As in Section 4.2, the \( \kappa \) angle of the oxygen tetrahedra is approximated by \( \pi/8 \). Since for magnetic fields along the [110] axis

\[ P_c (H \parallel [110]) = \frac{A_c}{2} \left( \frac{\chi^{mm}(T)}{\mu_{Sat}} \right)^2 H^2, \]  

(4.22)

the corresponding element of the para-magnetoelectric tensor reads as

\[ \beta_{cab} = A_c \left( \frac{\chi^{mm}(T)}{\mu_{Sat}} \right)^2. \]  

(4.23)
At $T = 20$ K, the magnetic susceptibility of Ba$_2$CoGe$_2$O$_7$ in the (001) plane is $\chi_T^{mm} = 0.13 \mu_B/T$ [193] and thus $\beta_{cab} = 0.35 \mu$Cm$^{-2}$T$^{-2}$, reproducing the result of the static magnetoelectric experiment.

To determine the other independent element of $\hat{\beta}$, one should align the external magnetic field along $b$ and consider the effect of a small orthogonal field along $c$. The emergent magnetoelectric polarization is

$$P_a = A_p \frac{\chi^{mm}_T(T)\chi^{mm}_c(T)}{(\mu_{Sat})^2} H_b H_c,$$  \hspace{1cm} (4.24)

resulting in

$$\beta_{abc} = A_p \frac{\chi^{mm}_T(T)\chi^{mm}_c(T)}{(\mu_{Sat})^2}.$$  \hspace{1cm} (4.25)

Using the susceptibility value $\chi^{mm}_c = 0.074 \mu_B/T$ [192] at $T = 20$ K, one gets $\beta_{abc} = 0.45 \mu$Cm$^{-2}$T$^{-2}$ for Ba$_2$CoGe$_2$O$_7$.

The absorption spectra of Ba$_2$CoGe$_2$O$_7$ at $T = 20$ K show directional dichroism, as presented in Fig. 4.14. Based on the magnetoelectric sum rule in Eq. 3.18, the differential $\chi^{me}(H) = c\beta H/2$ magnetoelectric susceptibility can be calculated and connected to the static results ($c$ stands for the speed of light in vacuum). I have studied the high temperature directional dichroism in various configurations to explore both independent elements of the $\hat{\beta}$ tensor.

In magnetic field along the [110] axis, the paramagnetic point group is 2$\Gamma_{[001]}m_{[110]}^m_{[110]}$, hence the material is expected to exhibit optical magnetoelectric effect for light propagation along [110]. If the oscillating magnetic and electric fields of light point along [110] and [001], respectively, the magnetoelectric contribution to the polarization is given by

$$P^\omega_c (H \parallel [110]) = \frac{1}{2} (-2\beta_{cab} - 2\beta_{cba}) \frac{HH^\omega}{2} = -\beta_{cab} HH^\omega,$$  \hspace{1cm} (4.26)

resulting in the directional dichroism shown in Fig. 4.14(b). Similarly, for perpendicular polarization of light, i.e., $H^\omega \parallel [001]$ and $E^\omega \parallel [110]$, the other element of $\hat{\beta}$ is probed, and oscillating magnetoelectric polarization along the 110 axis is induced:

$$P^\omega_{[110]} (H \parallel [110]) = \sqrt{2}P^\omega_a = \frac{\sqrt{2}}{2} (\beta_{abc} + \beta_{acb}) \frac{HH^\omega}{\sqrt{2}} = \beta_{abc} HH^\omega,$$  \hspace{1cm} (4.27)

responsible for the directional dichroism displayed in Fig. 4.14(a).

The same elements of $\hat{\beta}$ can be observed in magnetic fields along [100], when the 2$\Gamma_{[001]}^m_{[110]}$ paramagnetic symmetry allows magneto-chiral dichroism.
for light propagation parallel to the magnetic field. For $H^\omega \parallel [010]$ and $E^\omega \parallel [00\overline{1}]$ polarization, the oscillating magnetoelectric polarization can be calculated as

$$P_c^\omega (H \parallel [100]) = \frac{1}{2} (-\beta_{cab} - \beta_{cba}) HH^\omega = -\beta_{cab} HH^\omega. \quad (4.28)$$

Analogously for the perpendicular polarization state, $H^\omega \parallel [001]$ and $E^\omega \parallel [010]$,

$$P_b^\omega (H \parallel [100]) = \frac{1}{2} (\beta_{bac} + \beta_{bca}) HH^\omega = \beta_{abc} HH^\omega. \quad (4.29)$$

With the use of the ME sum rule in Eq. 3.18, the differential magnetoelectric susceptibility, $\chi^{me} = c\beta H/2$, can be calculated from each of the directional dichroism spectra, as presented in Fig 4.15. Based on the observed magnetic field dependence of $\chi^{me}$, the two independent components of $\beta$ are determined as $\beta_{cab} = 0.19 \mu\text{Cm}^{-2}\text{T}^{-1}$ and $\beta_{abc} = 0.29 \mu\text{Cm}^{-2}\text{T}^{-2}$. Within
Magnetic field dependence of the differential magnetoelectric susceptibility in the paramagnetic phase of Ba$_2$CoGe$_2$O$_7$ at $T = 20$ K $\approx 3T_N$, as calculated from the directional dichroism spectra using Eq. 3.18. The magnetic field was applied along the [110] (squares) and [100] (dots) axes. Light polarization is indicated in the graph. Lines show linear fits to the data.

In summary, in this chapter I described a detailed far-infrared optical study of the magnetoelectric Co-based melilite crystal family. These compounds exhibit various types of directional dichroism depending on the direction of the external magnetic field, in full agreement with the symmetry analysis in Chapter 2. I could show, that the non-reciprocal optical effect is not restricted to the low-temperature ordered phase, but survives in the paramagnetic phase as well. Comparing my optical spectra with former static ME results, I provided experimental support for the ME sum rule of...
Eq. 3.18. The magnetic field dependence of the resonance frequencies is non-trivial, although in one case I succeeded to describe the low-frequency modes of Ba$_2$CoGe$_2$O$_7$ by a classical mean-field model.
Chapter 5

Spin-wave excitations of TbFe$_3$(BO$_3$)$_4$

In this chapter I will discuss the evolution of the spin-wave excitations of multiferroic TbFe$_3$(BO$_3$)$_4$ with magnetic field. The magnetic ground state and the observed magnetic field dependence of the resonance frequencies can be understood in the framework of a mean-field spin model. Compared to former mean-field studies that were based solely on the static magnetization data [218–221], my model gives a quantitative description of both the ground-state spin texture and the low-energy spin excitations. The presentation of the experimental and theoretical results follows my work published in Ref. [222].

5.1 Rare-earth ferroborates

TbFe$_3$(BO$_3$)$_4$ belongs to a popular new family of magnetoelectric multiferroic crystals, the RFe$_3$(BO$_3$)$_4$ rare-earth ferroborates. Their unique crystal structure, possessing magnetic iron and rare-earth sites ($R$) in a chiral arrangement, allows the investigation of a wide variety of exotic magnetic and magnetoelectric phenomena. [218, 223–227]

Rare-earth ferroborates crystallize in the non-centrosymmetric, chiral R$_32$ structure, as seen in Fig. 5.1. The Fe$^{3+}$ ions are surrounded by edge-sharing O$^{2-}$ octahedra and form helical chains along the trigonal $c$ axis of the crystal. [228, 229] Most members of the rare-earth ferroborate family undergo a first order phase transition to the P$_{3}$$\bar{1}$2$\bar{1}$ structure. This symmetry lowering has an impact on the spin system, namely the Fe$^{3+}$ ions are no longer equivalent. One of the two iron sites—similarly to the iron sites of the R$_32$ structure—possesses local twofold rotational symmetry around the $a$ axis,
Figure 5.1: $R_{32}$ crystal structure of rare-earth ferroborates. Panel (a): Three consecutive $ab$ plane layers of iron (green) ions inside of oxygen (red) octahedra (green) and rare-earth (orange) ions inside oxygen prisms (orange). The dark yellow and blue oxygen equilateral triangles around the two crystallographically inequivalent boron atoms are spacers between the iron - rare-earth layers, and are displayed on the picture of both corresponding layers. Atoms marked by black circles are above each other. Panel (b): Three-dimensional view of the crystal structure containing three iron helices running along the $c$ axis.

while the other type of iron site has no rotational symmetry. One third of the iron sites belongs to the first type, the other two thirds to the second type. Correspondingly, there are two types of iron helices. [230, 231] The temperature of the $R_{32} \rightarrow P_{31} 21$ structural transition of rare-earth ferroborates ranges from $T_S = 58$ K($R = $ Eu) to $T_S = 350$ K($R = $ Y). Besides $R = $ Eu and Y, other compounds with $R = $ Gd ($T_S = 133 - 156$ K), Tb ($T_S = 198$ K) and Er ($T_S = 340$ K) undergo the same phase transition, while compounds with $R = $ Pr and Nd do not show this structural change. [232]

Iron helices along the $c$ axis are the building blocks of the magnetic structure. Along the helix, the neighbouring Fe magnetic moments are strongly coupled via short Fe-O-Fe exchange paths preferring an antiferromagnetic spin order along the helix. The helices are only weakly connected by the long Fe-O-O-Fe superexchange paths. [230] Therefore, the magnetic interaction between the iron chains and the rare-earth ions located between the iron helices play leading role in tuning the effective spatial dimensionality of the
magnetic system. The strong single-ion anisotropy of the rare earth spins is transmitted to the originally nearly-isotropic Fe spins via $J_{fd}$ exchange interactions. [225] The dominant magnetic interaction is the $J_{dd}$ exchange coupling between Fe spins, which leads to an antiferromagnetic ordering of the Fe subsystem. The rare earth spins—largely separated from each other—remain paramagnetic and are only polarized by the ordered Fe moments via the $J_{fd}$ exchange. [219, 233]

The strong spin-orbit coupling of the rare-earth ions plays a key role in the multiferroicity of these materials, i.e., their ME response is dominated by the rare-earth sites. [223, 224, 234] Correspondingly, the ME properties of rare-earth ferroborates can be efficiently tuned by the selection of different rare earth elements characterized by different magnetic anisotropies.

The $R=$Tb [219, 220], Pr [235] and Dy [236] members of the $R\text{Fe}_3(\text{BO}_3)_4$ family are easy axis antiferromagnets below their Néel temperatures ranging between $T_N = 30 - 40$ K. In magnetic fields parallel to the $c$ easy axis, these compounds show a spin-flop transition. In the spin-flop phase the $R$ moments align parallel to the magnetic field, while the Fe spins rotate into the $ab$ plane to gain more Zeeman energy via canting along the field. The spin-flop transition is accompanied by magnetostriction along the $c$ axis and a small jump in the electric polarization perpendicular to $c$, in the order of $\Delta P_a \approx 10 \mu\text{C/m}^2$. [226].

The less anisotropic $R=$Gd [233] and $R=$Ho [237] compounds also show easy-axis type antiferromagnetic behaviour below $T_N = 9$ K and 5 K, respectively, without any observable ferroelectric polarization.

On the other hand, the magnetic moments in the $R=$Nd [224, 238], Sm [239] and Eu [240] rare-earth ferroborates order antiferromagnetically in the $ab$ plane. In the magnetically ordered phase they show a significant ferroelectric polarization in the order of $\Delta P_a \approx 300 \mu\text{C/m}^2$, which is strongly magnetic field dependent. [226] The variation of the electric polarization is also accompanied by magnetostriction and changes in the dielectric constant. [226]

In the case of $R=$Er [241], the easy-plane type single-ion anisotropy of the rare-earth site is weaker, and together with the $R=$Gd [233] and $R=$Ho [237] members of the crystal family develops an easy plane magnetic order. In $\text{YFe}_3(\text{BO}_3)_4$, Y is non-magnetic, and the emerging antiferromagnetic order of the Fe system also shows a weak easy plane anisotropy. [237] The ferroelectric polarization of the above compounds is significantly smaller than for $R=$Nd, Sm or Eu, it ranges from zero (Er) to a few (Gd) $\mu\text{C/m}^2$. [226]
5.2 Magnetic order in TbFe$_3$(BO$_3$)$_4$

TbFe$_3$(BO$_3$)$_4$ is a particularly interesting member of the rare-earth ferroborate family. Due to the effect of the strong crystal field, the ground-state doublet of Tb$^{3+}$ ion is separated from the excited states by a considerable energy gap of 25 meV (6 THz).\cite{220, 242} Thus, at low temperatures the $S_{\text{Tb}} = 6$ spin of the Tb$^{3+}$ ion behaves like an Ising moment pointing along the trigonal $c$ axis of the crystal. As in the sister compounds $R=$Pr\cite{235} and $R=$Dy\cite{236}, in TbFe$_3$(BO$_3$)$_4$ the easy-axis anisotropy of the rare-earth ion is transmitted to the antiferromagnetic $S = \frac{5}{2}$ iron system. Consequently, TbFe$_3$(BO$_3$)$_4$ shows a collinear antiferromagnetic order below $T_N = 40$ K with all spins lying along the $c$ axis.\cite{219, 220, 240}

As mentioned before, magnetic fields along the $c$ axis induce spin-flop transition when all the Tb moments coalign with the field, while the sublattice magnetization of the antiferromagnetic Fe subsystem rotates to the $ab$ plane and a weak canting develops along the $c$ axis. The spin-flop transition field is $\mu_0H_{SF} = 3.5$ T at $T = 2$ K and increases with increasing temperature.\cite{219} The magnetic order of TbFe$_3$(BO$_3$)$_4$ was widely investigated by both magnetization and elastic neutron scattering experiments.\cite{219, 220} The temperature and field dependent behavior of the static magnetization was reproduced by former mean-field calculations\cite{220, 242}. However, the collective magnetic excitations of the ground state were only studied in zero magnetic field via optical spectroscopy.\cite{221}

I have investigated the low-energy magnetic excitations of TbFe$_3$(BO$_3$)$_4$ using far-infrared optical spectroscopy up to high magnetic fields applied along and perpendicular to the trigonal $c$ axis. I interpreted the observed field dependence of the resonance frequencies and the magnetization by a mean-field spin model. Earlier mean-field studies described the temperature dependence of either the static\cite{218–220} or the zero-field dynamic\cite{221} magnetic properties of TbFe$_3$(BO$_3$)$_4$ using free-energy approaches and approximating the Tb moments by Ising spins. All of these studies neglect the Tb-Fe exchange interaction for ions located in the same $ab$ plane. In contrast, my model allows a small canting of the quasi-Ising Tb moments and introduces a finite Tb-Fe exchange interaction for ions located in the same $ab$ plane to achieve a quantitative agreement with both the static and dynamic magnetic properties at zero temperature.
Figure 5.2: Magnetic field dependence of the low-frequency magnetic resonances in TbFe$_3$(BO$_3$)$_4$ at $T = 2$ K. In panel (a) and (c) the magnetic field points along the trigonal $c$ axis, while in panel (b) the field is perpendicular to the $c$ axis. Light propagation was always parallel or antiparallel to the applied field (Faraday geometry). Magnetic absorption and reflection spectra are vertically shifted in proportion to the applied magnetic field. In panel (a), blue and red absorption curves measured in the High Field Magnet Laboratory in Nijmegen (HFML) correspond to light propagation parallel and antiparallel to the magnetic field, respectively. Black absorption curves in all panels and green reflectivity spectra in panel (c) were measured on the TeslaFIR setup of the National Institute of Chemical Physics and Biophysics in Tallinn. Note that all absorption spectra in panels (a) and (c) were measured in the same measurement configuration, i.e. with $B \parallel c$ and unpolarized light beam. Insets of panels (a) and (b) show the weaker resonances of the corresponding spectra on a 10-times magnified absorption scale. Grey shaded lanes are guides for the eye. Precession of the iron spins (green) and ground state of terbium moments (orange) in the two phases is illustrated by arrows in panel (a).
5.3 Magnetic resonances of TbFe$_3$(BO$_3$)$_4$

5.3.1 Observed resonances

In Figs. 5.2(a)-(c), the optical absorption spectra measured at $T = 2$ K and in $\mu_0H = 0$ T reveal a clear resonance at $\omega_1 = 0.44$ THz. Though this resonance has already been observed and assigned as an antiferromagnetic resonance of the Fe system, [221] its field dependence has not been investigated so far.

In magnetic fields $H < H_{SF} = 3.5$ T parallel to the c axis the $\omega_1$ resonance shows a V-shape splitting to $\omega_{1A}$ and $\omega_{1B}$ modes, as followed in Figs. 5.2(a) and 5.2(c). Above $H_{SF}$ these resonances are replaced by a single mode, $\omega_{1C}$, which hardens linearly with increasing field. These resonances are also visible in the field dependence of the reflectivity spectra whose inverted line shape, dip in the reflectivity, as compared to the line shape of dielectric resonances, supports their magnetic nature.

Two further resonances with field independent $\omega_2 = 0.93$ THz and $\omega_3 = 1.17$ THz frequencies, best visible in Fig. 5.2(a), also appear in the spin-flop phase. Despite their constant frequencies, their oscillator strengths grow with increasing field, indicating the magnetic origin of these modes. Besides these pronounced resonances some weaker ones can also be observed in the low-field phase, as shown in the inset of Fig. 5.2(a). These resonance lines are located at $\omega_4 = 0.98$ THz and $\omega_5 = 1.26$ THz in $\mu_0H = 0$ T and also show a V-shape splitting with increasing magnetic field. The splitting has the same opening angle as found for the $\omega_1 = 0.44$ THz mode. The $\omega_4$ and $\omega_5$ resonances are observed in both set of my experiments performed in the High Field Magnet Laboratory in Nijmegen (HFML) and on the TeslaFIR setup of the National Institute of Chemical Physics and Biophysics in Tallinn, as shown in the inset of Fig. 5.2(a).

As expected for an easy axis antiferromagnet, the $\omega_1$ resonance exhibits a quadratic shift towards higher frequencies with increasing magnetic field applied perpendicular to the c axis, as shown in Fig. 5.2(b). The other excitation discernible in this configuration is the $\omega_4$ mode, whose frequency is nearly frequency independent in the range $\mu_0H = 0 - 12$ T although it gains oscillator strength with increasing magnetic field.

The temperature dependence of the $\omega_1$ resonance frequency in zero field shows the behavior expected for an anisotropic antiferromagnet, namely it gets softer and broader as the temperature approaches $T_N = 40$ K. My results measured in transmission and reflection geometries are in good agreement with the former study of A. M. Kuz’menko et al., [221] as shown in Fig. 5.3(c).
5.3.2 Seemingly contradicting absorption and reflection experiments

The weak $\omega_4$ and $\omega_5$ resonances, and the field independent $\omega_2$ and $\omega_3$ modes, although observed in absorption, are not visible in the reflectivity spectra of Fig. 5.2(c), while the stronger low frequency $\omega_{1A}$, $\omega_{1B}$ and $\omega_{1C}$ modes appear in both set of experiments. The reason of this difference is that absorption and reflectivity measurements have different sensitivity to detect the dynamic magnetic susceptibility depending on the frequency of light.

In case of low-frequency, purely magnetic excitations, if the electric excitations are at much higher frequency, the relative dielectric permittivity can be considered as a real constant $\varepsilon(\omega) \approx \varepsilon^\infty$, the optical absorption coefficient according to Eq. 3.7 is

$$\alpha(\omega) \approx \frac{\omega \sqrt{\varepsilon^\infty}}{c} \Im \chi^{mm}(\omega).$$  \hspace{1cm} (5.1)

The $\omega$ factor makes absorption experiments more sensitive to higher frequency magnetic excitations, contributing via the $\chi^{mm}(\omega)$ dynamic magnetic susceptibility.

On the other hand, the normal incidence reflectivity signal can be written as

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2$$

according to Fresnel’s formula. In the visible spectral range, where the relative magnetic permeability is unity, the Fresnel formula is simpler, namely $R(\omega) = |(N(\omega) - 1) / (N(\omega) + 1)|^2$. However, in the spectral range of spin-wave excitations, the relative magnetic permeability is $\mu(\omega) \approx 1 + \chi^{mm}(\omega)$. Since $|\chi^{mm}| \ll 1$, the reflectivity in first order of $\chi^{mm}(\omega)$ reads as

$$R(\omega) \approx R^0 - \frac{2 \sqrt{R^0} \varepsilon^\infty}{(\varepsilon^\infty + 1)^2} \Re \chi^{mm}(\omega),$$  \hspace{1cm} (5.3)

where

$$R^0 = \left| \frac{\sqrt{\varepsilon^\infty} - 1}{\sqrt{\varepsilon^\infty} + 1} \right|^2$$  \hspace{1cm} (5.4)

is the term corresponding to the background dielectric constant. Thus, the intensity of the magnetic reflectivity signal does not scale with the frequency, which makes the reflectivity experiment less sensitive for higher-frequency excitations as compared to absorption measurements.
The sensitivity of the reflectivity spectrum to a magnetic resonance is determined by the $2\sqrt{\varepsilon_\infty} / (\varepsilon_\infty + 1)^2$ prefactor, which has its maximum at

$$\varepsilon_{\text{ideal}} = \left(2 + \sqrt{3}\right)^2 \approx 13.93.$$

(5.5)

The dielectric permittivity of TbFe$_3$(BO$_3$)$_4$ in the 0.25 – 0.5 THz frequency range was determined in backward-wave tube experiments. [221] The $\varepsilon_{\text{ideal}} = 12.5$ and $\varepsilon_c = 13.5$ values for electric polarization in the $ab$-plane and along the $c$-axis, respectively, are quite close to $\varepsilon_{\text{ideal}}$, which explains why it is possible to observe the weak low-frequency magnetic excitations, $\omega_{1A}$, $\omega_{1B}$ and $\omega_{1C}$, in the normal incidence reflectivity spectra.

5.3.3 Understanding the lack of directional dichroism

I found that in TbFe$_3$(BO$_3$)$_4$, the absorption coefficient of magnetic excitations is the same for light propagation parallel and antiparallel to the magnetic field within the accuracy of the measurement. It means that despite the chiral crystal structure, the homochiral sample does not show considerable magneto-chiral dichroism (MChD) in the studied frequency window, which is surprising in the light of the symmetry analysis in Chapter 2.

On the other hand, static and dynamic magnetoelectric effects are closely related by the ME sum rule as discussed in Chapter 3. Static studies revealed that the magnetoelectric effect is mainly associated with Tb sites in TbFe$_3$(BO$_3$)$_4$. [234] Since dynamic ME susceptibility is responsible for the directional dichroism in the THz spectral range, the absence of MChD suggests that the observed excitations are of purely magnetic origin, and belong to the Fe subsystem. This is in accordance with the strong Ising character of the Tb moments, which act on the Fe spins as a static internal magnetic field but otherwise do not contribute to the spin dynamics. This implies that the excitations of the Tb moments, located at higher frequencies, should show directional dichroism. In contrast, a recent study [49] found strong directional dichroism in the easy-plane antiferromagnet Sm$_{0.5}$La$_{0.5}$Fe$_3$(BO$_3$)$_4$, which originates from the coupled dynamics of the rare-earth sites with magnetoelectric character and the Fe spins.

5.4 Classical mean-field model

Here I develop a classical mean-field model, which captures the magnetic field dependence of the ground state and that of the strong magnetic modes. I model the Fe and Tb moments, two sublattices for each, as classical vectors
Figure 5.3: Comparison of experiments and model calculations. (a) The red and blue curves are experimental magnetization data reproduced from [219] and [220], respectively, while black curves are the results of my classical Monte Carlo simulations. When the magnetic field $H$ is perpendicular to the trigonal $c$ axis the three lines coincide within the linewidth. (b) The magnetic field dependence of the low-frequency Fe resonances; symbols are used for the experimental data and lines for the simulation results. Black color is used when the magnetic field is parallel and blue when it is perpendicular to the trigonal axis. The nearly field-independent dashed mode was not observed in my Faraday geometry measurements (light propagation parallel to the magnetic field), but is allowed in the Voigt geometry (light propagation perpendicular to the magnetic field, oscillating magnetic field of light is parallel to the static magnetic field). Smaller symbols indicate additional weaker resonances. (c) Temperature dependence of the zero field resonance, as determined by my optical experiments (black squares), in backward-wave tube experiments [221] (gray circles), and as calculated (solid black line) from the temperature dependence of the length of the magnetic moments [219] according to Eq. 5.9.

with different lengths, $\frac{5}{2}$ for Fe ($S_{FeA}$ and $S_{FeB}$) and 6 for Tb moments ($S_{TbA}$ and $S_{TbB}$). The energy of a single magnetic unit cell can be written as:
\[
\mathcal{H} = \Lambda \left( (S_{\text{TbA}}^x)^2 + (S_{\text{TbB}}^x)^2 \right) - 6J_{dd}S_{\text{FeA}}S_{\text{FeB}} \\
- 6J_{fd1}(S_{\text{FeA}}S_{\text{TbB}} + S_{\text{FeB}}S_{\text{TbA}}) - 3J_{fd2}(S_{\text{FeA}}S_{\text{TbA}} + S_{\text{FeB}}S_{\text{TbB}}) \\
- 3g_{\text{Fe}}\mu_0\mu_B H (S_{\text{FeA}} + S_{\text{FeB}}) - g_{\text{Tb}}\mu_0\mu_B H (S_{\text{TbA}} + S_{\text{TbB}}).
\tag{5.6}
\]

We include a strong negative uniaxial single-ion anisotropy term \(\Lambda\) for the Tb sites to model their Ising-like nature. In case of the terms describing the exchange energy contributions, numeric prefactors correspond to the coordination numbers. An isotropic negative \(J_{dd}\) exchange term connecting the Fe sublattices is responsible for the antiferromagnetic order. It is reasonable to consider the magnetic anisotropy of the rare-earth system only since in \(\text{YFe}_3(\text{BO}_3)_4\) and \(\text{GdFe}_3(\text{BO}_3)_4\) with non-magnetic or magnetically isotropic rare-earth site, respectively, the Fe spin system is nearly isotropic Heisenberg-like. \[243\]

The Tb and Fe moments are coupled by the \(J_{fd1}\) and \(J_{fd2}\) exchange terms, where the dominant \(J_{fd1}\) connects moments on adjacent \(ab\) layers and the weaker \(J_{fd2}\) links ions on the same \(ab\) layers. This kind of coupling was neglected so far, \([218, 220, 242]\) since the superexchange path corresponding to \(J_{fd2}\) is quite long.

The last two terms of Eq. 5.6 describe the Zeeman energy, where \(H\) is the external magnetic field.

### 5.4.1 Estimation of model parameters based on magnetization data

Approximate values for the parameters in Eq. 5.6 can be deducted from the static magnetization data and can be further tuned to fit the lowest excitation frequencies of the system. For the first estimation of the exchange and anisotropy constants I used the Landé values \(g_{\text{Fe}} = 2\) and \(g_{\text{Tb}} = 1.5\) given for the free ions, which could be modified by crystal-field effects. Due to the strong crystal field on the Tb site one can expect \(g_{\text{Tb}}\) to deviate from the Landé value. The Fe\(^{3+}\) ion has only spin moment, thus, it is expected to preserve the \(g_{\text{Fe}} = 2\) g-factor.

The slope of the magnetization in \(H > H_{SF}\) magnetic field parallel to the \(c\) axis is governed by the susceptibility of the Fe subsystem, because in the spin-flop phase all the Tb moments point along the magnetic field, hence, do not contribute to the susceptibility. The susceptibility per formula unit \(\chi_{mm}^{nn} = 0.12 \pm 0.01 \mu_{\text{B}} T^{-1}\) is determined by the \(J_{dd}\) exchange, hence \(J_{dd} \approx -\frac{3g_{\text{Fe}}}{2\chi_{mm}^{nn}} = -2.9 \pm 0.3\) meV. \([219, 220]\) This value of \(J_{dd}\) is in good agreement
with most of the previous studies \((J_{dd} \approx -2.1 \text{ meV}, -3.3 \text{ meV}, -3 \text{ meV})\). \([219, 220, 242]\)

At the spin-flop transition the \(S_{\text{TbB}}\) moments occupying one half of the Tb sites flip from \(S_{\text{TbB}}^c = -6\) to \(S_{\text{TbB}}^c = 6\), giving rise to a \(6g_{\text{Tb}}\) jump in the magnetization per formula unit. In addition, the Fe moments show some canting in the spin-flop phase, which also gives a minor contribution to the jump in the magnetization. The spin-flop transition takes place when the energy of the collinear and spin flop phases are equal, resulting in an approximate expression for the Tb-Fe coupling:

\[
J_{fd1} - J_{fd2}/2 \approx \frac{g_{\text{Tb}}\mu_0\mu_B H_{SF}}{15} + \frac{(5 + 4g_{\text{Tb}})\mu_0^2\mu_B^2 H_{SF}^2}{900} \chi_{\text{c}}^{mm},
\]

where higher order terms in \(\chi_{\text{c}}^{mm}\) are neglected. Due to the different exchange paths \(|J_{fd2}/2|\) is expected to be much smaller than \(|J_{fd1}|\). Correspondingly, all of the previous studies in the literature neglected the contribution of \(J_{fd2}\) and attributed the whole Tb-Fe coupling to the \(J_{fd1}\) exchange coupling. \([220, 242]\) On the other hand, static magnetization data are not sufficient to unambiguously determine both \(J_{fd1}\) and \(J_{fd2}\), thus, in this section \(J_{fd2} = 0\) is assumed following previous works.

The effective field along the \(c\) axis acting on the antiferromagnetic Fe system can be approximated by the sum of the external field and the effective field of the Tb moments. Since in the spin-flop phase both of the Tb sublattices are in the \(S_{\text{TbB}}^c = 6\) state, their effective field on the Fe site is \(\frac{6}{g_{\text{Tb}}\mu_B} (J_{fd1} + J_{fd2}/2) \approx \frac{6}{g_{\text{Tb}}\mu_B} J_{fd1} = \frac{4g_{\text{Tb}}}{g_{\text{Fe}}} \mu_0 H_{SF} = 2.1 \text{ T}\). Thus, the \(\Delta M^c = 9.1 \pm 0.1 \mu_B\) magnetization jump \([219, 220]\) at the spin-flop transition is

\[
\Delta M^c (H_{SF}) = 6g_{\text{Tb}} + \chi_{\text{c}}^{mm} \left( \mu_0 H_{SF} + \frac{6 (J_{fd1} + J_{fd2}/2)}{g_{\text{Tb}}\mu_B} \right)
\]

\[
\approx 6g_{\text{Tb}} + \chi_{\text{c}}^{mm} \mu_0 H_{SF} \left( 1 + \frac{4g_{\text{Tb}}}{g_{\text{Fe}}} \right),
\]

giving rise to a refined value of \(g_{\text{Tb}} \approx 1.405 \pm 0.025\) which is significantly lower than the \(g_{\text{Tb}} = 1.5\) Landé value. Neutron scattering studies \([219]\) reported \(g_{\text{Tb}} S_{\text{Tb}}^c = 8.53\mu_B\) ordered Tb moment at \(T = 2\text{ K}\), corresponding to \(g_{\text{Tb}} = 1.42\), which is in good accordance with my analysis.

Using Eq. 5.7 the strength of the Tb-Fe exchange can be determined, \(J_{fd1} \approx 0.04 \pm 0.0013\text{ meV}\). This is in good agreement with the 0.044 meV and 0.039 meV values of previous magnetization studies. \([218, 220]\) The same coupling constant was determined from the splitting of the ground quasi-doublet of the Tb ions, which was observed as a splitting of the infrared transitions, corresponding to 0.045 meV. \([242]\)
Table 5.1: Parameters of Eq. 5.6 obtained by fitting the static magnetization data [219, 220] (first row) and refined parameters using both magnetization and magnetic resonance data (second row). Rows 3–6: corresponding parameters of previous mean-field studies, all of which neglecting $J_{fd2}$. In the column of the Tb single-ion anisotropy $\Lambda$ upper and lower error bars are indicated by + and – values, respectively. Ref. [242] uses crystal field theory to reproduce all the energies of the electronic excitations of the Tb$^{3+}$ ion. To compare the set of crystal field parameters of Ref. [242] to the single $\Lambda_{eff}$ anisotropy term of my simplified approach, I converted them to a single $\Lambda_{eff}$, which provides the best match between the crystal field energy levels of the $L=3, S=3, J=6$ subspace and the $\Lambda_{eff} (S_{Tb}^e)^2 − 15 (J_{fd1} − J_{fd2}/2) S_{Tb}^e$ energies for the set of $S_{Tb}^e \in \{-6,..,6\}$. The model of Ref. [218], [221] also includes a weak easy-plane type single-ion anisotropy for the Fe sites, $\Lambda_{Fe}$, which would correspond to a $3\Lambda_{Fe} ((S_{FeA}^e)^2 + (S_{FeB}^e)^2)$ energy term in Eq. 5.6.

<table>
<thead>
<tr>
<th>$g_{Fe}$</th>
<th>$g_{Tb}$</th>
<th>$J_{dd}$ [meV]</th>
<th>$J_{fd1}$ [meV]</th>
<th>$J_{fd2}$ [meV]</th>
<th>$\Lambda$ [meV]</th>
<th>$\Lambda_{Fe}$ [meV]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.405 ± 0.025</td>
<td>−2.9 ± 0.26</td>
<td>0.04 ± 0.0013</td>
<td>0</td>
<td>$-4.1^{+1.6}_{-6.2}$</td>
<td>0</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>1.365 ± 0.025</td>
<td>−2.67 ± 0.15</td>
<td>0.054 ± 0.004</td>
<td>0.026 ± 0.009</td>
<td>$-8.1^{+3.6}_{-3.0}$</td>
<td>0</td>
<td>this work</td>
</tr>
<tr>
<td>2</td>
<td>1.42</td>
<td>−3.27</td>
<td>0.048</td>
<td>0</td>
<td>$-\infty$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.47</td>
<td>−2.1</td>
<td>0.043</td>
<td>0</td>
<td>$-\infty$</td>
<td>0</td>
<td>[219]</td>
</tr>
<tr>
<td>2</td>
<td>1.46</td>
<td>−2.69</td>
<td>0.041</td>
<td>0</td>
<td>$-\infty$</td>
<td>0.008</td>
<td>[218, 221]</td>
</tr>
<tr>
<td>2</td>
<td>1.46</td>
<td>−3</td>
<td>0.045</td>
<td>0</td>
<td>$\Lambda_{eff} \approx -2.5$</td>
<td>0</td>
<td>[242]</td>
</tr>
</tbody>
</table>
For fields perpendicular to the \( c \) axis, the susceptibility of the system is \( \chi_{ab}^{mm} = 0.14 \pm 0.002 \mu_B/T \), which is about 20% larger than \( \chi_c^{mm} \). \([219, 220]\) As the Fe system is expected to be isotropic, the anisotropy of the susceptibility indicates the small canting of the Tb moments and thus can be used to estimate the anisotropy of the Tb sites: \( \Lambda \approx -\frac{g_{Tb} \chi_{ab}^{mm}}{2(\chi_{ab}^{mm} - \chi_c^{mm})} = -4.1^{+1.6}_{-0.2} \) meV (upper and lower error bars are indicated by + and −, respectively). The uncertainty of \( \Lambda \) comes from the variation of the experimental values for \( \chi_{ab}^{mm} \) and \( \chi_c^{mm} \). However, due to the length of the Tb moments, \( \Lambda (S_{Tb}^c)^2 \) gives the dominant energy scale of the system in the studied magnetic field range. This justifies the approximation that Tb moments behave almost like Ising spins. The values obtained for \( \Lambda \) correspond to the range of the lowest excited crystal field energy levels calculated for the Tb\(^3+\) ion. \([242]\]

The model parameter set obtained above is presented in the first row of Table 5.1, which reproduces the static magnetization data. However, the static magnetization data only supports a rough estimation of the model parameters. Moreover, in the former expressions only one combination of the two types of Tb-Fe coupling appears, namely \( J_{fd1} - J_{fd2}/2 \), and therefore in studies based on the magnetization data the minor \( J_{fd2} \) was simply neglected. \([220, 242]\) In the following, using the magnetic field dependence of the dominant low-frequency magnetic excitations I will determine \( J_{fd1} \) and \( J_{fd2} \) separately and refine the values of all parameters in the Hamiltonian in Eq. 5.6.

5.4.2 Determination of model parameters based on magnetic resonances

Assuming Ising-like Tb moments (\( \Lambda \to -\infty \)), I calculated the zero temperature resonance frequencies of the Fe system following the more general approach of Ref. \([215]\) using the \( S_{Tb} = 6 \) and \( S_{Fe} = \frac{5}{2} \) values:

\[
\omega_1 (H = 0) = \sqrt{\left( \left( J_{fd1} - \frac{J_{fd2}}{2} \right) S_{Tb} \right)^2 - 2J_{dd}S_{Fe} \left( J_{fd1} - \frac{J_{fd2}}{2} \right) S_{Tb}} \tag{5.9}
\]

\[
\omega_{1A/B} (H = H^c < H_{SF}) = \omega_1 \pm g_{Fe} \mu_0 \mu_B H \tag{5.10}
\]

\[
\omega_{1C} (H = H^c > H_{SF}) = \left( J_{fd1} + \frac{J_{fd2}}{2} \right) S_{Tb} + g_{Fe} \mu_0 \mu_B H \tag{5.11}
\]

\[
\omega_1 (H = H^{ab}) = \sqrt{\omega_1^2 + (g_{Fe} \mu_0 \mu_B H)^2}. \tag{5.12}
\]

Equations 5.9-5.12 can be easily understood in an effective field approach. The effective magnetic field producing the anisotropy at the iron sites in
zero external magnetic field is $g_{Fe}\mu_0\mu_B H_{An} = (J_{fd1} - J_{fd2}/2) S_{Tb}$, while the effective field of the iron-iron exchange is $g_{Fe}\mu_0\mu_B H_{Ex} = -2J_{dd}\mu_0 S_{Fe}$, both parallel to the $c$ axis of the crystal. The zero-field resonance of the effective field model corresponds to the geometric mean of the above two fields, $g_{Fe}\mu_0\mu_B \sqrt{H_{Ex} H_{An}} = g_{Fe}\mu_0\mu_B H_{EA} \approx \omega_1 (H = 0)$. The resonance frequency is the same for the two iron sublattices, i.e., both of them can be considered to precess in a $H_{EA}$ effective field. Their effective fields point in opposite directions along the $c$ axis. When a $H$ external magnetic field along the $c$ axis is applied, the equivalence of the iron sublattices is broken, they feel $H_{EA} \pm H$ effective field resulting in precession frequencies of Eq. 5.10. On the other hand, external field in the $ab$-plane is perpendicular to $H_{EA}$, thus they sum up according to the Pythagorean theorem, yielding Eq. 5.12 for the precession frequency of both iron sublattices. In the spin-flop phase, due to the flip of the Tb moments the effective anisotropy field is changed to $g_{Fe}\mu_0\mu_B H_{An}^{SF} = (J_{fd1} + J_{fd2}/2) S_{Tb}$, which is perpendicular to the antiferromagnetic iron order. Without this anisotropy the whole iron system could collectively rotate in the $ab$-plane without any energy cost, realizing a Goldstone excitation [244]. The precession of the whole antiferromagnetic iron system is gapped by the sum of $H_{An}^{SF}$ and the parallel external field, giving the resonance frequency of Eq. 5.11. One restricting limitation of the above discussed effective field approach is that it substitutes a complicated potential by an effective Zeeman term and consequently is not able to account for anisotropies perpendicular to the effective field.

Using Eq. 5.9, the $J_{dd}$ Fe-Fe exchange can be determined with higher accuracy than the previous estimation from the $\chi_m^{mm}$ magnetic susceptibility. Based on the experimental $\omega_1 (H = 0) = 0.442 \pm 0.005$ THz frequency value one gets $J_{dd} = -2.67 \pm 0.15$ meV.

In the spin flop phase at $H^c = H_{SF}$ the effective magnetic field acting on the antiferromagnetic Fe system is $H_{SF} + \frac{6}{g_{Fe} \mu_B} (J_{fd1} + J_{fd2}/2)$, giving information about the sum of $J_{fd1}$ and $J_{fd2}$, thus can be used to unambiguously determine $J_{fd2}$. The experimental value of the $\omega_{1C}$ resonance frequency in the spin-flop phase can be extrapolated to $\omega_{1C} (H^c = H_{SF}) = 195$ GHz, corresponding to an effective field of $\mu_0 H = 7$ T. This results in $J_{fd1} = 0.054$ meV and $J_{fd2} = 0.026$ meV, and refines the Tb g-factor to $g_{Tb} = 1.365$ according to Eq. 5.8a. The $J_{fd2}$ exchange is indeed weaker than $J_{fd1}$, as expected, but it does not have a ferromagnetic character, in contrast to former expectations based on the crystal and magnetic structure. [219] Thus, in the zero-field ground state the bond corresponding to $J_{fd2}$ is frustrated.

According to Eqs. 5.10 and 5.11, the slope of the $\omega_{1A}$, $\omega_{1B}$ and $\omega_{1C}$ modes yields the $g$-factor of the Fe system, which within the error of the measurement is equal to the spin-only $g = 2$ value. Using Eq. 5.12 to fit the
resonance frequencies measured in the $H \perp c$ case I get the same $g$-factor, thus, the spin-only Fe $g$-factor is isotropic, as expected.

When considering the finite-temperature excitations of the system, in the zero field case Eq. 5.9 remains valid, only the temperature dependence of the lengths of the $S_{Tb}$ and $S_{Fe}$ ordered moments needs to be taken into account. However, a mean-field model like Eq. 5.6 is not able to properly describe the temperature dependence of the magnetic properties due to neglected thermal fluctuations, thus, for a quantitative description additional experimental input is needed. In the elastic neutron scattering studies [219] the lengths of the $S_{Tb}$ and $S_{Fe}$ ordered moments were reported in the whole temperature range of the antiferromagnetic phase. By substituting these temperature dependent ordered moments into Eq. 5.9 the temperature dependence of the zero field resonance I could reproduce with $g_{Fe} = 2$, $J_{dd} = -2.67$ meV, $J_{fd1} = 0.054$ meV and $J_{fd2} = 0.026$ meV, as shown in Fig. 5.3(c). Earlier backward-wave oscillator spectroscopy studies [221] reported the same temperature dependence.

For finite values of the Tb single-ion anisotropy $\Lambda$, the analytical solutions corresponding to Eqs. 5.9-5.12 are too complicated and I calculated the field dependence of the zero temperature resonances numerically. I used a classical Monte Carlo approach to find the minimal energy configuration of the four-spin system. Starting from random initial states, in each iteration step one of the magnetic moment vectors was rotated around a random axis by a small $\phi$ angle. The change was kept, if it lowered the energy of the system, while it was rejected otherwise. This method, converges to a local energy minimum if $\phi$ is slightly reduced in each step. The global minimum was found as the minimum of local energy minima obtained by starting the iteration from different random initial vectors. The resonance frequencies were determined by taking the eigenvalues of a matrix constructed from the second partial derivatives of the Hamiltonian in Eq. 5.6 in the ground state with respect to the spin Cartesian coordinates. The Tb single-ion anisotropy was set to

$$\Lambda \approx -\frac{g_{Tb}}{2(\chi_{mm}^{\text{ub}} + \frac{3g_{Fe}}{2J_{dd}})} = -8.1 \text{ meV},$$

(5.13)

and the other exchange parameters used in the simulation are compared to earlier studies [218–221, 242] in Table 5.1. The calculated field dependence of the magnetization and antiferromagnetic resonance frequencies reproduce the experimental curves, as shown in Figs. 5.3(a) and 5.3(b). With finite $\Lambda$ the Tb moments are not static any more but oscillate with a zero-field resonance frequency of $\omega_{Tb} = \Lambda S_{Tb} = 50$ meV, which agrees well with the frequency range of 25-50 meV, the range of the lowest excited crystal field energy levels calculated for the Tb$^{3+}$ ion. [242] Considering my experimental
results summarized on Fig. 5.2, the inclusion of a finite $\Lambda$ term does not alter the Fe resonance frequencies much. It is necessary only to reproduce the anisotropy of the static magnetic susceptibility.

The field independent $\omega_2$ and $\omega_3$ resonances and the weak $\omega_4$ and $\omega_5$ modes cannot be explained by this simple classical four-sublattice mean-field spin model. The splitting of $\omega_4$ and $\omega_5$ corresponds to a $g$-factor of 2, indicating that they belong to the Fe subsystem. Their presence shows that the Fe sites are crystallographically not equivalent, as is expected for the low-temperature $P3_121$ space group $[230, 231]$ of TbFe$_3$(BO$_3$)$_4$. Thus, the proper description of the magnetic resonances is possible only with six magnetic Fe sublattices which are connected by various non-equivalent Fe-O-Fe intrachain and Fe-O-B-O-Fe interchain superexchange paths. Distinction between intrachain and interchain coupling would allow the tuning of the dimensionality of the system, thus the Monte Carlo approach could probably also reproduce the magnetic properties and resonance frequencies at finite temperatures. Nevertheless, due to the weak structural distortion from the room-temperature $R32$ structure to the low-temperature $P3_121$, the magnetic properties can be approximated by assuming crystallographically equivalent Fe sites.

As discussed in section 3.2.2, the intensities of magnetic resonances can be quantitatively connected to the static magnetic susceptibility. In Fig. 5.4 the temperature dependence of the zero field $\chi^{m}_{ab}$ susceptibility is shown, as measured in static experiments [219, 220] and as calculated from the observed intensity [221] of the $\omega_1$ resonance when the oscillating magnetic field was in the $ab$ plane. As seen in the figure, error bars of the susceptibility calculated from my optical data does not allow us to draw conclusions from the comparison of static measurements and integrals of optical spectra. However, at least both the static and dynamic methods used to determine the magnetic susceptibility agree within the experimental error with my mean field calculations.

In conclusion, I showed that the field dependence of the resonance frequencies and the magnetization data [219, 220] give complementary information about the studied magnetic system. In order to reproduce both sets of data, I developed a classical mean-field spin model, which quantitatively describes the main features in field dependence of the magnetization [219, 220] and that of the resonance frequencies with a minimal set of magnetic interactions including exchange couplings and single-ion anisotropy. My far-infrared experiments also indicated that the magnetic structure of TbFe$_3$(BO$_3$)$_4$ is more complicated than previously believed. There are six inequivalent magnetic Fe sublattices, thus a more detailed neutron diffraction study is necessary to clarify the real magnetic ground state.
Figure 5.4: Temperature dependence of the $\chi_{ab}$ static magnetic susceptibility. Green dashed [220] and red dotted [219] lines are the results of static experiments. The upturn of the green line at higher temperatures is explained by a few degrees misalignment of the sample. Blue line and black dots are calculated from the temperature dependence of the intensity of the $\omega_1$ mode measured by means of backward-wave tube technique [221] and far-infrared optical spectroscopy (my data), respectively. In all dynamic measurements the oscillating magnetic field was in the $ab$ plane. Error bars of my experimental data correspond to the standard deviation of the measured intensities at 4 K in five different configurations. My mean field calculation for the $\chi_{ab}$ static magnetic susceptibility, which is expected to be temperature independent in the magnetically ordered phase, is shown by orange short-dashed line.
Summary

The major achievement of my Ph.D. research are summarized in the following points:

1. Using symmetry considerations, I identified the crystallographic magnetic point groups, where non-reciprocal directional anisotropy, i.e. inequivalence of propagation or absorption of particles or waves along opposite directions, can emerge. Specific to optical spectroscopy, I proposed a large collection of candidate materials, which can potentially exhibit such phenomena for all polarization state of light. Besides the mechanisms already reported in the literature, I predicted a novel type of directional anisotropy. [P1]

2. Based on statistical physical considerations I have derived a sum rule relation connecting the static magnetolectric susceptibility to the difference between the integral of the two absorption spectra corresponding to counter-propagating light beams. I validated the magnetolectric sum rule by comparing the static and dynamic magnetolectric responses of the magnetolectric Co-based melilites, Ba$_2$CoGe$_2$O$_7$ and Ca$_2$CoSi$_2$O$_7$, in various experimental configurations. [P2]

3. In order to determine the relevant magnetic interactions in Ba$_2$CoGe$_2$O$_7$ and Ca$_2$CoSi$_2$O$_7$, I performed a detailed far-infrared optical study of the spin-wave resonances in their antiferromagnetically ordered states. I verified that the magnetic field dependence of the lowest-frequency spin-wave resonances of Ba$_2$CoGe$_2$O$_7$ can be reproduced by classical mean-field theory and determined the value of the isotropic exchange coupling, the exchange anisotropy and the single-ion anisotropy. I have observed strong non-reciprocal magneto-chiral dichroism effect in high magnetic fields for both compounds. [P3, P4, P5]

4. Using symmetry analysis and the magnetolectric sum rule, I have predicted that the non-reciprocal directional anisotropy is not restricted to materials with long-range magnetic order, but can also emerge in
the paramagnetic state of non-centrosymmetric crystals. For the first time, I observed this optical para-magne
etoelectric effect in the spin excitations of Ba$_2$CoGe$_2$O$_7$.

5. I performed a detailed far-infrared optical study of the spin-wave resonances in the antiferromagnetic phase of TbFe$_3$(BO$_3$)$_4$. I developed a classical spin-wave theory which reproduces the magnetic field dependence of the magnetization as well as the frequency of the main spin-wave resonances. The presence of additional weaker excitations in the spin-wave excitation spectrum implies that the magnetic structure of TbFe$_3$(BO$_3$)$_4$ is more complicated than previously believed, with at least six inequivalent magnetic iron sublattices. [P6]
List of publications

Publications related to thesis points

[P1] D. Szaller, S. Bordács and I. Kézsmárki, 
*Symmetry conditions for nonreciprocal light propagation in magnetic crystals* 

[P2] D. Szaller, S. Bordács, V. Kocsis, T. Rõõm, U. Nagel and I. Kézsmárki, 
*Effect of spin excitations with simultaneous magnetic- and electric-dipole character on the static magnetoelectric properties of multiferroic materials* 

*One-way transparency of four-coloured spin-wave excitations in multiferroic materials* 

*Chirality of matter shows up via spin excitations* 
Nat. Phys. 8, 734 (2012).

*Spin-Stretching Modes in Anisotropic Magnets: Spin-Wave Excitations in the Multiferroic Ba$_2$CoGe$_2$O$_7* 
*Magnetic resonances of multiferroic TbFe$_3$(BO$_3$)$_4*

**Further publications**

*Evolution of two-dimensional antiferromagnetism with temperature and magnetic field in multiferroic Ba$_2$CoGe$_2$O$_7*

*Lattice modes and the Jahn-Teller ferroelectric transition of GaV$_4$S$_8*

*Spin excitations in the skyrmion host Cu$_2$OSeO$_3*

*Malaria pigment crystals as magnetic micro-rotors: Key for high-sensitivity diagnosis*
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