**In-situ electric field control of THz non-reciprocal directional dichroism in the multiferroic Ba$_2$CoGe$_2$O$_7$**

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Non-reciprocal directional dichroism, also called the optical-diode effect, is an appealing functional property inherent to the large class of non-centrosymmetric magnets. However, the in-situ electric control of this phenomenon is challenging as it requires a set of conditions to be fulfilled: Special symmetries of the magnetic ground state, spin-excitations with comparable magnetic- and electric-dipole activity and switchable electric polarization. We demonstrate the isothermal electric switch between domains of Ba$_2$CoGe$_2$O$_7$ possessing opposite magnetoelectric susceptibilities. Combining THz spectroscopy and multiboson spin-wave analysis, we show that unbalancing the population of antiferromagnetic domains generates the non-reciprocal light absorption of spin excitations.

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The interaction between light and matter may produce fascinating phenomena. Among them is the non-reciprocal directional dichroism (NDD), when the absorption differs for the propagation of light along and opposite to a specific direction. In contrast to the magnetic circular dichroism, the absorption difference for NDD is finite even for unpolarized light. The chirality of the light lies at the heart of the phenomenon: the electric ($E$) and magnetic ($H$) field components of the light and its propagation vector $k \propto E \times H$ form a right-handed system. Applying orthogonal static electric ($E$) and magnetic ($H$) fields to a material breaks the inversion and time-reversal symmetries, leading to the observation of NDD [1]. Such a symmetry breaking is inherent to magnetoelectric (ME) multiferroics, materials with coexisting electric and magnetic orders. In multiferroics, the ME coupling establishes a connection between responses to electric and magnetic fields: an external electric field generates magnetization $M$, and a magnetic field induces electric polarization $P$ in the sample. The NDD is manifested by the refractive index difference $\Delta N = N_+ - N_-$ for counter-propagating ($\pm k$) linearly polarized beams [2–4]. In the long-wavelength limit

$$N_\pm = \sqrt{\varepsilon_{\alpha\alpha} \mu_{\beta\beta}} \pm \chi_{\alpha\beta}^{em},$$ (1)

where $\varepsilon_{\alpha\alpha}$ and $\mu_{\beta\beta}$ are the components of the permittivity and the permeability tensors for oscillating fields polarized along $E^\omega_\alpha$ & $H^\omega_\beta$, and $\chi_{\alpha\beta}^{em}$ is the ME susceptibility characterizing the induced polarization $\delta P^\omega_{\alpha} \propto \chi_{\alpha\beta}^{em} H^\omega_\beta$. The $\chi_{\alpha\beta}^{em}$ becomes resonantly enhanced for spin excitations of multiferroics endowed with a mixed magnetic and electric dipole character giving rise to strong NDD [2–9].

Since $\Delta N \propto \chi_{\alpha\beta}^{em}$, the absorbing and transparent directions are determined by the sign of ME susceptibility, and therefore, they can be interchanged by the sign reversal of the $\chi_{\alpha\beta}^{em}$. The magnetic field can naturally switch between time-reversed magnetic states with opposite signs of ME responses, and allows the control of NDD [2–4]. Can we achieve a similar switch with an electric field, which is a time-reversal even quantity? Apart from being a fundamental question, the voltage control of NDD may promote the application of multiferroics in GHz–THz frequency data transmission and signal processing devices with reduced size and energy consumption. In addition to the NDD, the electric field induced switching between time-reversed magnetic states would also provide an efficient way to control other optical ME effects, such as chirality of magnons [9,10,11] or axion-term-induced gyrotropy [12]. The ME coupling may help us to achieve the desired control of magnetic states [5,7,13,16], how-
ever realizing this effect is not at all trivial. It requires a magnetic order permitting NDD and a polarization that is switchable by laboratory electric fields. In the visible spectral range, the realization of this effect has been confirmed for charge excitations [14, 15]. However, studies in the THz range of spin-wave excitations are scarce. So far, mostly ME poling was used to select between states in the THz range of spin-wave excitations are scarce. However, a small perturbation such as tilting of the field away from the polarization observed upon tilting the field away from the tetragonal axis induces an in-plane electric polarization $\delta P$ (light blue arrows) via linear magnetoelectric effect.

The clue how to control the NDD using electric fields comes from the experiment of Murakawa et al. [24]. They showed that a magnetic field applied nearly parallel to the tetragonal axis induces an in-plane electric polarization along one of the (100) directions. The hysteresis of the polarization observed upon tilting the field away from the [001] axis suggests a rearrangement of the magnetic domain population. The AFM order reduces the space group symmetry from $P2_1_2_1_2_1$ to $P2_1'$, corresponding to the breaking of the rotoreflection symmetry $I$, and the formation of four magnetic domains, shown in Fig. 1 (b) [22]. The $P2_1'2_12_1'$ symmetry gives rise to a finite $\chi^{\text{EEM}}$ and in a magnetic field $H \parallel [001]$ a polarization $\delta P$ parallel to the $L$ develops, as shown in Fig. 1(b). If the field is perfectly aligned $H \parallel [001]$, the four domains remain equivalent and the field-induced polarizations $\delta P$ cancel out. However, a small perturbation such as tilting of the magnetic field or applying an in-plane electric field can break the delicate balance between the domains. In our experiments, we exploit this highly susceptible state to change the relative population of the domains by electric field, $E \parallel [100]$, and attain control over the NDD, present for $E \times H$.

Ba$_2$CoGe$_2$O$_7$ single crystals were grown by the floating zone technique as described in [23]. Silver paste electrodes were painted on the parallel sides of a 2x3x0.7 mm$^3$ rectangular (010) cut. The THz spectra were measured in Tallinn with a Martin-Puplett interferometer and a 0.3 K
Our main experimental results are summarized in Fig. 2. Panel (a) displays the average and (b) the difference of the THz absorption spectra measured in electric fields with opposite signs $(E=\pm 3 \text{kV/cm})$ and constant magnetic fields. In agreement with former results [26], we assign the absorption peak around 18 cm$^{-1}$ (mode #1) to the optical magnon excitation of the easy-plane AFM ground state whereas resonances #2, #3 and #4, showing a V-shape splitting in magnetic fields, are attributed to the spin stretching modes involving the modulation of the spin length. In a finite magnetic field, the absorption spectra become different for the opposite signs of the electric field as evidenced by Fig. 2(b) for the light polarization $E^\perp \parallel [001]$ and $H^\perp \parallel [100]$. The electric field odd component of the signal is the manifestation of the NDD and it shows that the absorption is different for light propagation along or opposite to the cross-product of the static electric and magnetic fields $\mathbf{E} \times \mathbf{H}$. This relation is further supported by the fact that the differential absorption spectra change sign under the reversal of the external magnetic field. The NDD is finite only for the spin stretching modes #2 and #3 and it increases with magnetic fields up to $\sim 12 \text{T}$. We note that for the orthogonal light polarization, $E^\perp \parallel [001]$ and $H^\perp \parallel [001]$, we did not find electric field induced absorption difference within the accuracy of the experiment.

The electric field induced change in the absorption spectra around mode #3, measured with respect to the zero field cooled state, is displayed in Fig. 3(a). The peak absorption, shown in Fig. 3(b), depends on the electric field history of the sample: the initial and the following upward and downward sweeps are all different and the absorption difference has a small but finite remanence [34]. Furthermore, the electric field can change the absorption only below $T_N$ as displayed in Fig. 3(c), though the intensity of the spin stretching mode remains finite even above $T_N$ [2]. All of these findings suggest that the observed electric field effect arises only in the magnetically ordered phase and it is related to switching between domain states possessing different NDD.

Considering the symmetries of the zero-field ground state shown in Fig. 1(a), the (unitary) $2_1$ screw axis restricts NDD for light propagation $\mathbf{k} \parallel \mathbf{L}$ in a given domain. When a magnetic field is applied along $H \parallel [001]$, only the $2'_1$ symmetry remains. The $S^b$, $S^c$, $P^a$ operators are even, while $S^a$, $P^b$, $P^c$ are odd under $2'_1$ in domain I, depicted in Fig. 1(a). Since time reversal makes this symmetry antiunitary, the operators are either even or odd under conjugation, restricting the transition matrix elements to be either real or imaginary [44, 58]. As a consequence, the real part of a ME susceptibility combined from an even and odd operator vanishes, annuling the time-reversal odd part of $\chi^m_{bc}$ and $\chi^m_{ab}$, thus forbidding NDD when $k \parallel H \parallel [100]$. The $2'_1$ does not affect NDD in the other propagation directions, and indeed this is what we observed for $k \parallel [010]$. In finite fields, we also expect NDD for the $k \parallel [001]$ — but then the analysis of results would be more complicated as the Faraday effect mixes the polarization states of the light.

In order to interpret the experimental results quanti-
The electric dipole matrix elements are evaluated similarly for polarization components \( \tilde{P}_\alpha \). The ME susceptibility, \( \chi^{em}_{ca} \propto \langle 0 | \tilde{P}_\alpha | \alpha \rangle | \langle \alpha | S_a | 0 \rangle \), is plotted in Fig. 2(d).

For light polarization \( \mathbf{E}^\omega \parallel [001] \) and \( \mathbf{H}^\omega \parallel [100] \), our model predicts that two spin stretching modes have finite ME susceptibility \( \chi^{em}_{ca} \) and correspondingly show NDD with the same sign. The overall sign of the ME response is reversed upon the reversal of either the static electric or the magnetic field related to the switching from domain I to III. All of these findings are in agreement with the experiments and imply that the electric field control of the NDD is realized by influencing the AFM domains. We note that among modes #3 and #4, which show a tiny splitting in high fields, resonance #3 is NDD active in the experiment, whereas our theory predicts NDD for the higher energy mode. However, we found no obvious way to reproduce the fine structure of the resonance energies within our model or by including other realistic terms [21, 24, 25].

Although theory predicts that individual domains possess a finite dichroism as \( H_c \rightarrow 0 \) [see Fig. 3(b)], we observed vanishing NDD in this limit. This suggests that domain walls relax toward their initial positions and the domain population even as fields go to zero. The multidomain state may be favored by: (i) electric dipole-dipole interaction between the ferroelectric domains; (ii) elastic energy, since the AFM domains break the tetragonal symmetry they can couple to orthorhombic distortion [34]. The finite intensity of mode #1 also indicates that domains II & IV coexist with domain I & III. In domain I & III, excitation #1 is silent for this light polarization according to the calculation, since it can only be excited by the \( \mathbf{H}^\omega \parallel [010] \), which is perpendicular to \( \mathbf{L} \parallel [100] \). The polarization matrix element is also negligible for this resonance. Therefore, domains II & IV with finite magnetic dipole strength for \( \mathbf{H}^\omega \parallel [100] \) [see Fig. 2(c)] should also be present in the studied sample. Thus, one expects even stronger NDD than observed experimentally here, if the mono-domain state of either domain I or domain III can be realized. Finally, we note that the small difference in the averaged absorption [Fig. 2(a)] observed for the reversal of the magnetic field is probably caused by a small misalignment. When the magnetic field is slightly tilted toward the light propagation \( \mathbf{k} \parallel [010] \), the balance between domain I and III can be broken.

The absence of the NDD for the orthogonal light polarization, \( \mathbf{E}^\omega \parallel [100] \) and \( \mathbf{H}^\omega \parallel [001] \), can be explained by the smallness of the \( \chi^{em}_{ac} \). Due to the nearly preserved O(2) symmetry of the system, the magnetic matrix element in \( \chi^{em}_{ac} \) involves the \( \tilde{S}^c \), which commutes with the terms of the Hamiltonian in Eq. 3 except for the \( \mathbf{E} \cdot \mathbf{P} \). Therefore the dipole oscillator strength for \( S^c \) – given by the double commutator [37] – is tiny compared to other matrix elements.

FIG. 3. (a) The electric field induced change in the absorption spectra measured with respect to the zero field cooled state at 3.5 K and in fixed magnetic field 12 T. (b) The hysteresis of the electric field dependence of the peak absorption. The horizontal arrows connect corresponding points of panels (a) and (b). (c) Temperature dependence of the electric field induced change in the absorption spectra measured in 12 T.
In summary, we demonstrated the isothermal voltage control of the non-reciprocal THz absorption in Ba$_2$CoGe$_2$O$_7$. In contrast to former studies applied ME poling, here the ME polarization is induced by a magnetic field preserving the nearly degenerate ground states within the tetragonal plane. This manifold allows efficient voltage control of the magnetic domain population and so of the NDD. A similar mechanism may give rise to NDD in ME spin-spiral compounds e.g. Cu$_2$OSeO$_3$ or CoCr$_3$O$_4$ with multi-domain states. Our results can promote the applications of multiferroics in voltage-controlled high-frequency devices and stimulate search for compounds with stronger remanence and higher ordering temperatures.

Note added: During the preparation of this manuscript, we become aware of the related work of Kimura et al., who study the electric field control of microwave NDD of the triplet Bose-condensate in TiCuCl$_3$ [38].

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Supplementary material: In Situ Electric Field Control of THz Nonreciprocal Directional Dichroism in the Multiferroic Ba$_2$CoGe$_2$O$_7$

I. MAGNETOELECTRIC ANNEALING

To study the effect of magnetoelectric (ME) annealing (poling), we cooled the sample from 10 K to 3.5 K in the presence of electric, $E_{\text{poling}}$ and magnetic fields $H_{\text{poling}}$. At low temperature we measured the THz absorption in finite electric, $E$ and magnetic fields $H$. The magnitude of the electric and magnetic fields applied for annealing or during the measurements were 3 kV/cm and 8 T, respectively. When we turned off the fields the domain population became nearly uniform as discussed in the main text.

The difference of the absorption spectra measured in $E=+E_{\text{poling}}$ with opposite signs at a fixed $H_{\text{poling}}$ right after cooling to 3.5 K are shown in red and blue in Fig. S1. After the annealing we reversed the electric field at low temperature and measured the absorption difference again. Orange and green curves are recorded for $\mu_0 H_{\text{poling}}=+8$ T and positive and negative poling electric fields, respectively. Dark cyan and magenta curves are measured for $\mu_0 H_{\text{poling}}=-8$ T and positive and negative poling electric fields, respectively. The absorption difference is almost identical for ME annealing and in situ reversal of the electric fields. These measurements confirm that at low temperature we can control the antiferromagnetic domains as much as the ME term allows.

II. SELECTION RULES OF THE MAGNETOELECTRIC SUSCEPTIBILITY

In this section we provide details for the symmetry classification of magnetization and electric polarization operators that determine the NDD response in the ordered state. The classification uses the symmetries of the antiferromagnetically ordered state in Ba$_2$CoGe$_2$O$_7$ first in zero, then in finite magnetic field applied along the [001] direction, corresponding to the experiments.

Here we choose the directions of the coordinate axes in spin and polarization space according to the crystallographic ones, i.e. $a||[100]$, $b||[010]$, and $c||[001]$.

Zero external magnetic field

Without external magnetic field the generators of the magnetic space group in the domain I [shown in Fig. 1(a) in the main text] are isomorphic to the magnetic point group

$$\left\{\mathcal{S}, \{C_2^a|0\frac{1}{2}0\}, \{\Theta C_2^a|0\frac{1}{2}0\}\right\} \simeq \left\{\mathcal{S}, \Theta C_2^a, \Theta C_2^a, \Theta C_2^a\right\}. \quad (S1)$$
This magnetic (non-unitary) point group is called $22'2'$ or $D_2(C_2)$. The operators with a tilde will exchange sites $A$ and $B$ and $\Theta$ denotes the time reversal operation.

Let us denote the uniform components of the magnetization and polarization by

$$M = S_A + S_B,$$

and the staggered components by

$$L = S_A - S_B,$$

$$\Pi = P_A - P_B,$$

where $S_A$ is the spin on site $A$, $P_A$ is the polarization on site $A$, and so on. The polarization components are

$$P_j^a \propto - \cos 2\kappa_j (S_j^a S_j^c + S_j^c S_j^a) + \sin 2\kappa_j (S_j^b S_j^c + S_j^c S_j^b),$$

$$P_j^b \propto - \cos 2\kappa_j (S_j^a S_j^c + S_j^c S_j^a) - \sin 2\kappa_j (S_j^b S_j^c + S_j^c S_j^b),$$

$$P_j^c \propto - \cos 2\kappa_j (S_j^a S_j^b + S_j^b S_j^a) + \sin 2\kappa_j ((S_j^a)^2 - (S_j^b)^2),$$

where $j = A, B$ denotes the sublattices, and the tilt angles of the tetrahedra are $\kappa_A = - \kappa_B = \kappa$. The transformation properties of the site indices, position vectors and the spins and polarizations are collected in Table II.

The irreducible representations of the $D_2(C_2)$ group together with the classification of the net and staggered spin and polarization components are collected in Table III. As expected, the $M^b$, $L^a$, and $\Pi^c$ are invariant, so even without an external magnetic field both canted antiferromagnetism and antiferro-polarization is allowed in domain I [see in Fig. 1(a) in the main text].

The dynamical susceptibility responsible for the NDD is given by

$$\chi^{em}(\omega) \propto \sum_n \Re(\langle 0|P^n|n\rangle \langle n|M^v|0\rangle)\delta(\omega - E_n + E_0),$$

where $u, v$ take the $a, b, c$ values, $|0\rangle$ is the ground state and the $|n\rangle$'s are excited states. We will get non-zero susceptibility if both $P^a$ and $M^v$ transform according to the same irreducible representation. In Table III we have collected the possible combinations for different directions of light. It turns out that in zero field we may expect finite signal only for light propagation along $[010]$. We shall also note that since the Hamiltonian is almost $O(2)$ symmetric about the $[001]$ axis, the $M^c$ almost commutes with the Hamiltonian (it commutes with the most significant $J, J^c$ and $\Lambda$ terms), and the matrix element $\langle n|M^c|0\rangle$ is small. The $\chi^{em}_{ac}(\omega)$ only gets contribution from the small in-plane anistropy and therefore it is much smaller than $\chi^{em}_{ca}(\omega)$.

**Finite external magnetic field $H || [001]$**

If we apply an external field pointing in the $c$ direction, only the

$$\left\{\mathbf{\mathcal{P}}, \{\Theta C_2^{\|/2}00\}\right\} \cong \{\mathbf{\mathcal{P}}, \Theta C_2^{\|/2}\}$$

**Table II.** Character table and transformation properties of the uniform and staggered magnetization and polarization components in the absence of external fields. $A_1$ is the identity irreducible representation.

| Irrep | $\mathcal{P}$ | $\Theta C_2^{\|/2}$ | $\Theta C_a^{\|/2}$ | $\Theta C_2^{\|/2}$ |
|-------|---------------|----------------|-----------------|----------------|
| $A_1$ | 1             | 1             | 1              | 1             |
| $A_2$ | 1             | 1             | -1             | -1            |
| $B_1$ | 1             | -1            | 1              | -1            |
| $B_2$ | 1             | -1            | -1             | 1             |

**Table III.** Matrix elements in zero external magnetic field, based on the character table of $D_2(C_2)$. Table III. Since the magnetic and electric components of the light are perpendicular, the cases when $H^\| || E^\|$ are meaningless and are denoted by crosses ($\times$).

| $H^\| || [001]$ | $H^\| || [010]$ | $H^\| || [001]$ |
|-----------------|-----------------|-----------------|
| $E^\| || [001]$ | $B_1$           | finite (small)  |
| $E^\| || [010]$ | $A_2$           | 0               |
| $E^\| || [001]$ | $B_2$           | finite          |

Irreps.
generators remain. This magnetic point group is the $2'$ or $C_2(C_1)$, with the unitary group element being just the identity. There are only two irreps, $A_1$ and $A_2$, and the classification of the uniform and staggered spin and polarization components is shown in Table IV.

Noting that the time-reversal operator can be expressed as $\Theta = C_2K$ in the diagonal $S^c$ basis, where $K$ is the operator of complex conjugation, we can simplify the anti-unitary $\Theta \tilde{C}_2$ operator as follows:

$$\Theta \tilde{C}_2 = C_2^bK\tilde{C}_2 = C_2^b(\tilde{C}_2^c)^*K = C_2^b\tilde{C}_2K = \tilde{C}_2^cK$$ \hspace{1cm} (S7)

where we used that $\tilde{C}_2^c = \tilde{C}_2^c$ and we introduced the unitary $\tilde{C}_2^c = C_2^b\tilde{C}_2$, with the property $\tilde{C}_2^c)^{-1} = \tilde{C}_2^c$. The transformation $\Theta \tilde{C}_2\{O\}$ for matrices is now $(\tilde{C}_2^cK)O(\tilde{C}_2^cK)^{-1}$ and we can write

$$(\tilde{C}_2^cK)O(\tilde{C}_2^cK)^{-1} = \tilde{C}_2^cKO(\tilde{C}_2^cK)^{-1} \tilde{C}_2^c = \tilde{C}_2^cO^*\tilde{C}_2^c. \hspace{1cm} (S8)$$

When we consider the effect of the $\Theta \tilde{C}_2\{O\} = \pm O$ symmetry on the matrix elements of physical observables, we find that all representations are even or odd, following Table IV. In matrix representation, using Eq. (S8):

$$\tilde{C}_2^cO^*\tilde{C}_2^c = \pm O. \hspace{1cm} (S9)$$

Let us apply Eq. (S9) to the operators in the $\langle 0|P^u|n\rangle\langle n|M^v|0\rangle$ matrix elements for the dynamical susceptibility, Eq. (S5):

$$\langle 0|\tilde{C}_2^c(P^u)^*\tilde{C}_2^c|n\rangle\langle n|M^v\tilde{C}_2^c|0\rangle = \langle 0|\pm\tilde{P}^u|n\rangle\langle n|\pm\tilde{M}^v|0\rangle \hspace{1cm} (S13)$$

Using the transformation properties of the eigenstates given by Eq. (S12), we get

$$\langle 0|\tilde{P}^u|n\rangle\langle n|M^v|0\rangle = (\pm)P_+^u(\pm)M_-^v\langle 0|P^u|n\rangle\langle n|M^v|0\rangle. \hspace{1cm} (S14)$$

Let us apply Eq. (S9) to the operators in the $\langle 0|P^u|n\rangle\langle n|M^v|0\rangle$ matrix elements for the dynamical susceptibility, Eq. (S5):

$$\langle 0|\tilde{C}_2^c(P^u)^*\tilde{C}_2^c|n\rangle\langle n|M^v\tilde{C}_2^c|0\rangle = \langle 0|\pm\tilde{P}^u|n\rangle\langle n|\pm\tilde{M}^v|0\rangle \hspace{1cm} (S13)$$

Using the transformation properties of the eigenstates given by Eq. (S12), we get

$$\langle 0|\tilde{P}^u|n\rangle\langle n|M^v|0\rangle = (\pm)P_+^u(\pm)M_-^v\langle 0|P^u|n\rangle\langle n|M^v|0\rangle. \hspace{1cm} (S14)$$

**Table IV.** Character table and transformation properties of net and staggered spin and polarization components, when the external magnetic field points in the $z$ direction.

| Irrep | $\tilde{C}_2^c$ | $\Theta \tilde{C}_2^c$ | Operators |
|-------|----------------|----------------------|-----------|
| $A_1$ | 1              | 1                    | $M^b$, $M^c$, $L^a$, $P^a$, $\Pi^b$, $\Pi^c$ |
| $A_2$ | 1              | -1                   | $M^a$, $L^b$, $L^c$, $\Pi^a$, $P^b$, $P^c$ |

**Table V.** Magnetoelastic susceptibility $\chi^{em}(\omega)$ in finite external magnetic field $||[001]$ in the domain I for different light directions and polarizations, based on the character table for $2'$. Each entry in the table contains two data: the type of the configuration (Faraday or Voigt), and the information about the existence (and magnitude) of the appropriate susceptibility component. Our experimental setup corresponds to the Voigt geometry set in boldface.

| irrep | $H^\parallel[[100]]$ | $H^\parallel[[010]]$ | $H^\parallel[[001]]$ |
|-------|---------------------|---------------------|---------------------|
| $E^{+}[[100]]$ | $A_1$ | $\times$ | Faraday finite | Voigt finite (small) |
| $E^{+}[[010]]$ | $A_2$ | Faraday finite | $\times$ | Voigt 0 |
| $E^{+}[[001]]$ | $A_2$ | Voigt finite | 0 | $\times$ |

This restricts the matrix elements of the $\chi^{em}(\omega)$ to be real when both $P^u$ and $M^v$ belong to the same irreducible representation of the $2'$ magnetic point group, and to be pure imaginary when they belong to different irreducible representations – in this case we do not expect NDD signal. These selection rules are collected in Table V.