

## Symmetry conditions for nonreciprocal light propagation in magnetic crystals

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Recent studies demonstrated the violation of reciprocity in optical processes in low-symmetry magnetic crystals. In these crystals the speed of light can be different for counterpropagating beams. Correspondingly, they can show strong directional anisotropies such as direction dependent absorption also called directional dichroism [Bordács *et al.*, *Nat. Phys.* **8**, 734 (2012); Saito *et al.*, *J. Phys. Soc. Jpn.* **77**, 013705 (2008)]. Based on symmetry considerations, we identify the magnetic point groups of materials which can host such directional anisotropies and also provide a list of possible candidate materials to observe these phenomena. In most of these cases, the symmetry of the crystal allows directional anisotropy not only for optical processes but also for the propagation of beams of particles and scalar waves. We also predict new types of directional optical anisotropies—besides the toroidal-moment-induced optical magnetoelectric effect and the magnetochiral dichroism investigated so far—and specify the magnetic point groups of crystals where they can emerge.

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When a measured quantity of matter 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 reciprocity as a synonym of time reversal symmetry,<sup>1</sup> later it was generalized by also considering spatial symmetries of the studied system.<sup>2</sup> A rigorous definition of reciprocity for scattering processes has been recently given by Deák and Fülöp.<sup>3</sup>

Specific to optical phenomena, among reciprocity-violating media we consider those which can distinguish between counterpropagating light beams irrespective of the polarization state of the light, i.e., we say a material shows directional anisotropy when such nonreciprocity is present for each polarization of the light beam. As a counterexample, we recall the well-known Faraday effect when the nonreciprocity holds for circularly and elliptically polarized light.<sup>4,5</sup> However, for linearly polarized incident beams traveling through a transparent magnetic medium, irrespective of their propagation directions (forward or backward), the transmitted beams have the same linear polarization in the laboratory frame of reference.<sup>6</sup> In this case the reciprocity is violated for certain but not all polarizations, thus, in our term the corresponding media show no directional anisotropy.

Although the presence of such reciprocity-violating directional anisotropy in the properties of bulk matter may seem strange and counterintuitive, it has been recently verified in a large variety of low-symmetry materials. In an absorbing medium this directional anisotropy results in different strengths of absorption for beams traveling along opposite directions which is called directional dichroism. Similar directional optical phenomena—schematically shown in Fig. 1—have already been observed for emission,<sup>7,8</sup> absorption,<sup>9</sup> and diffraction<sup>10</sup> of light in materials belonging to two different symmetry classes where the directional optical phenomena are manifested in the corresponding two configurations.

The optical magnetoelectric effect (OME) was observed in systems with finite ferrotoroidic moment<sup>11</sup>—which can arise

in simple cases 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.<sup>9</sup> Instead of reversing the light propagation, the sign of the toroidal moment was switched to be parallel and antiparallel to the velocity of light. A remarkable portion of the absorption was found to be an 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<sub>3</sub> in the x-ray absorption of the core electron excitations<sup>12</sup> and for absorption due to intra-atomic *d-d* transitions over the visible-ultraviolet spectral range.<sup>13,14</sup> Enhancement of OME in diffraction was observed using a grating made of the same compound.<sup>14</sup> Metamaterials composed of two-dimensional ferromagnetic islands with polar shape can also host OME in diffraction.<sup>15</sup>

Materials without spontaneous electric polarization and/or magnetization can show OME as well if a toroidal moment  $\mathbf{T}$  is induced by crossed static electric and magnetic fields, as was observed for the electronic *f-f* transitions of Er<sup>3+</sup> in Er<sub>1.5</sub>Y<sub>1.5</sub>Al<sub>5</sub>O<sub>12</sub><sup>16</sup> and in Er-doped ferroelectric (Ba,Sr)TiO<sub>3</sub>.<sup>17</sup> Besides the usual case discussed above, spontaneous toroidal moment can also be present in antiferroelectric and/or antiferromagnetic compounds, whenever  $\mathbf{t} = \sum_i \mathbf{r}_i \times \mathbf{m}_i$  is finite,<sup>18</sup> while  $\mathbf{T}$  can be vanishing. Here  $\mathbf{m}_i$  and  $\mathbf{r}_i$ , 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<sup>19–21</sup> can produce such  $\mathbf{t}$  toroidal moment without finite  $\mathbf{T}$ .

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 (via a finite gate-channel potential), showed a difference for current flowing along or opposite to the toroidal moment.<sup>22</sup> Directional anisotropy was predicted recently for

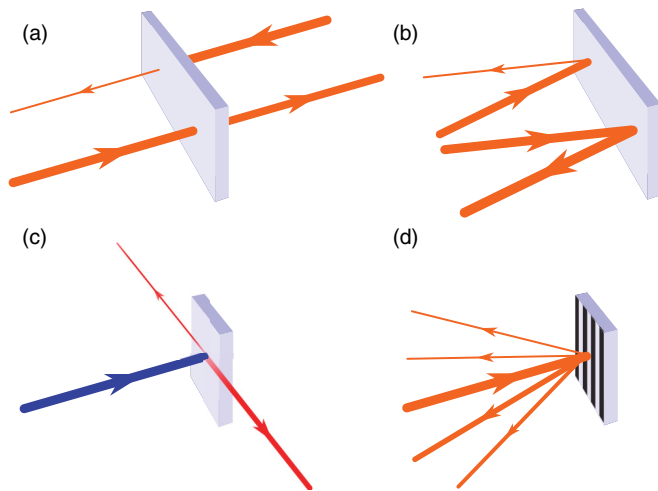


FIG. 1. (Color online) Schematic representation of direction-dependent light propagation in (a) transmission, (b) reflection, (c) emission, and (d) Bragg scattering. In case of (a) transmission and (b) reflection, forward and backward propagating beams distinguished by the medium are simultaneously shown. (c) Excitations by higher energy photons (blue arrow) decay via emission characterized by direction-dependent emission rates (red arrows). (d) Equal intensity for beams diffracted symmetrically to the direct beam is broken by directional anisotropy.

the propagation of spin waves in planar magnonic crystals with metallic overlayers and dielectric underlayers<sup>23</sup> and in an ultrathin Fe film on a W(110) surface.<sup>24</sup> The latter was experimentally observed by spin-polarized electron energy loss spectroscopy.<sup>25</sup> In both cases the 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/reflection/diffraction or in electric resistance, gave small relative directional differences in the range of  $10^{-5}$ – $10^{-2}$ . Recent experiments on magnetoelectric multiferroic materials show a relative OME in the order of unity as it was demonstrated for intra-atomic  $d$ - $d$  transitions of  $\text{CuB}_2\text{O}_4$  in the near-infrared spectral region<sup>26</sup> and in the electromagnon spectrum of  $\text{Ba}_2\text{CoGe}_2\text{O}_7$  in the THz photon frequency range,<sup>27</sup> which may bring the possibility of their optical applications, e.g., as magnetically controlled directional light switches.

The second type of optical directional anisotropy effect, the magnetochiral 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  $\text{Eu}[(\pm)\text{tfc}]_3$  complex,<sup>7,8</sup> 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  $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ <sup>28</sup> and in the enantioselective photochemical dissociation of chiral complexes.<sup>29</sup> A similar phenomenon, the difference in the phase retardations of counterpropagating light beams, was found in chiral organic liquids.<sup>30,31</sup> The emergence of MChD was also demonstrated

in Bragg scattering.<sup>10</sup> 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 magnetochiral anisotropy was observed in helically distorted bismuth stripes<sup>32</sup> and also in chiral carbon nanotubes.<sup>33</sup> In all these cases the directional anisotropy was rather weak corresponding to a relative difference of  $10^{-8}$ – $10^{-2}$  in the studied quantities. Similar to the case of OME, multiferroic materials can also show a significant MChD effect in both their infrared  $d$ - $d$  excitations<sup>34</sup> and spin-wave absorption spectra.<sup>35</sup>

Motivated by the recently observed plethora of directional anisotropy effects and their potential in future applications using multiferroic compounds, we study the general symmetry conditions allowing directional anisotropy in optical phenomena. Our focus is on crystalline materials where we systematically identify those crystallographic magnetic point groups which can support directional anisotropy effects. Besides the symmetry conditions where OME and MChD can be realized, we found additional magnetic symmetry groups which can host new types of directional anisotropy effects. These new directional effects are specific to crystalline media in contrast to OME and MChD which can also emerge in the optical properties of gases, liquids, and amorphous solids.

When neglecting the weak interaction, light-matter interaction possesses time reversal<sup>36</sup> ( $\tau$ ) and full  $O(3)$  spatial symmetry, in other words transformation of the whole “light source-sample-detector system” by  $\tau \otimes O(3)$  symmetry operations must not change the interaction process. Therefore, only the crystallographic and magnetic structure of matter can give constraints to the symmetry of the measured optical quantities. Using Neumann’s principle these constraints can provide relations between the tensor elements describing the linear optical response such as 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 symmetry of the material. Thus, every symmetry elements, which could convert any of the optical processes into their reversed pairs, need to be eliminated from the magnetic point group of such crystal.

According to our definition, directional anisotropy is allowed for a given propagation direction in a material, if no symmetry operation of the crystal can transform a light beam (of any polarization) traveling along this direction into a counterpropagating one without changing its polarization state. Conservation of the polarization means that the path of the electric polarization vector determines the same curve in the laboratory frame upon forward and backward propagation. As a necessary condition, the material must lack spatial inversion and time reversal symmetries because they convert counterpropagating beams with the same linear polarization into each other. To systematically determine the conditions of directional anisotropy in a crystal we have to consider each element of the corresponding magnetic point group. Let us take a beam with arbitrary elliptical polarization propagating along the  $z$  axis. Since the electric displacement and magnetic flux density vectors ( $\mathbf{D}$  and  $\mathbf{B}$ , respectively) lie in the  $xy$  plane we only need to treat those orthogonal transformations

which leave this plane invariant. In crystals these are the  $n$ -fold proper ( $n$ ) and improper ( $\bar{n}$ ) rotations around the  $z$  axis for  $n = 1, 2, 3, 4$ , and  $6$  and around an axis laying in the  $xy$  plane for  $n = 1$  and  $2$ . All of these operations can be combined with the reversal of time which will be denoted by a prime ( $'$ ). In this paper an improper rotation means a proper rotation combined with spatial inversion, giving  $\bar{1}$  for the spatial inversion and  $\bar{2}$  for a mirror plane symmetry.

As long as we consider the propagation of unpolarized light, the necessary 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 opposite 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 operation 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 ( $\bar{n}'$ ) around the  $z$  axis meet this criterion for any  $n \in \{1, 2, 3, 4, 6\}$ . Besides that  $\bar{2}$  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 the  $xy$  plane invariant—the propagation along the  $+z$  and  $-z$  directions can be different not only for unpolarized light but for other unpolarized or scalar waves (e.g., acoustic waves) and 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  $\bar{n}$  and  $n'$  reverse the propagation of light. Both transformations rotate the axes of the polarization ellipse by  $\frac{2\pi}{n}$ . While  $n'$  transposes clockwise and counterclockwise circulation of the polarization,  $\bar{n}$  preserves the sense of circulation in the laboratory frame. Since the direction of propagation is reversed,  $n'$  will preserve and  $\bar{n}$  will change the the sense of circulation in the frame of the light beam. For  $n = 1$  and  $2$ ,  $n'$  connects every elliptical polarization state with its counterpropagating pair, and  $\bar{n}$  does the same for linearly polarized states. Thus, both prohibit directional optical anisotropy (in our term) as at least for specific polarizations the propagation direction is reversed and the polarization in the light frame is kept intact. For  $n = 3$  the  $n$ -times repetition of  $n'$  and  $\bar{n}$  results in  $1'$  and  $\bar{1}$ , respectively, and for  $n = 6$  the  $\frac{n}{2}$ -times repetition of  $n'$  and  $\bar{n}$  gives  $2'$  and  $\bar{2}$ , respectively, which all forbid directional anisotropy. In contrast, for  $n = 4$  no power of  $\bar{4}$  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 counterpropagating pair.

Among the operations around an axis lying in the  $xy$  plane only  $1', \bar{1}, 2$ , and  $\bar{2}'$  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  $(\bar{n})^l$  results either in  $2$  or  $\bar{2}'$  depending on the parity of  $l$ . For  $n = 4l$ ,  $(n')^{2l} = (\bar{n})^{2l} = 2$  and for  $n = 2l + 1$ ,  $(n')^n = 1'$  and  $(\bar{n})^n = \bar{1}$ . Therefore, the presence of  $2l, \bar{2}l', 4l', \bar{4}l', (2l + 1)'$ , or  $\bar{2}l + \bar{1}$  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 the previous 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  $\bar{4}$  which allows directional anisotropy for any light polarization except for unpolarized light where the difference cancels out.

Table I lists the crystallographic magnetic point groups except those which contain the time reversal or spatial inversion symmetry. We 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 propagation vector of light.

A static toroidal moment ( $\mathbf{T}$  or  $\mathbf{t}$ ) transforms under all possible symmetry operations identically to the wave vector since the latter is the cross product of the electric and magnetic components of light. 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 the OME. The magnetic point groups compatible with  $\mathbf{T}$ —denoted by T in Table I—are subgroups of the symmetry group of a perpendicular magnetic and electric field vector  $2'mm'$ , where the electric field is parallel to  $2'$ , magnetic field is perpendicular to the mirror plane  $m$  and  $\mathbf{T}$  points perpendicular to the plane  $m'$ . In the notation of the magnetic point groups we follow the international convention, where  $m$  stands for mirror plane symmetry. The toroidal moment  $\mathbf{t}$  can arise without the presence of electric polarization and magnetization, thus,  $\mathbf{t}$  is compatible with higher symmetry point groups than  $\mathbf{T}$ . Indeed,  $\mathbf{t}$  can exist the same point groups where a general time reversal odd polar vector can appear. In the case of crystals these are the subgroups of  $n/m'mm$  and  $\bar{n}'2'm$ , where  $\mathbf{t}$  is parallel to the principal axis and  $n = 4$  or  $6$ . Since a spontaneous, nondissipative electric current<sup>65</sup> has the same symmetry properties as  $\mathbf{t}$ , they can be present in the same 31 crystallographic magnetic point groups. These groups are labeled with t in Table I.

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 vector 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 MChD and is indicated by MC in Table I.

TABLE I. Crystallographic magnetic point groups and possible configurations for directional anisotropy (DA). We omitted the point groups which contain the  $1'$  time reversal or  $\bar{1}$  spatial inversion operation. After the international symbol of each point group the symmetry allowed magnetic structure (F is ferromagnetic, AF is antiferromagnetic) is indicated. 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  $T$  and  $t$ , (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 multiferroic crystals belonging to the given magnetic point group are given in the fifth and tenth columns, where  $B_\alpha$  stands for an external magnetic field pointing to the  $\alpha$  crystallographic direction.

Crystal system	International notation	DA		Materials	Crystal system	International notation	DA		Materials
		$\parallel$ to PA	$\perp$ to PA				$\parallel$ to PA	$\perp$ to PA	
Triclinic	1 (F)	T, MC, t	T, MC, t	Ba <sub>2</sub> Ni <sub>7</sub> F <sub>18</sub> <sup>37</sup>	Rhombohedral	3 (F)	MC, P, t	X	Cu <sub>2</sub> OSeO <sub>3</sub> $B_{[111]}$ <sup>19,a</sup>
	$\bar{1}$ (AF)	T, t	–			$\bar{3}$ (AF)	t	X	Cr <sub>2</sub> O <sub>3</sub> <sup>59</sup>
Monoclinic	$m$ (F)	–	T, t	BiFeO <sub>3</sub> $B_{[1\bar{1}0]}$ <sup>38,b</sup>		$3m$ (AF)	P, t	X	BiTeI $B_{[001]}$ <sup>41</sup>
	$m'$ (F)	T, t	–	Ni <sub>3</sub> B <sub>7</sub> O <sub>13</sub> I <sup>40,c</sup>		$3m'$ (F)	–	X	
	2 (F)	MC, P, t	–	BaNiF <sub>4</sub> <sup>42,d</sup>		32 (AF)	–	X	
	2' (F)	–	T, MC, t	LiCoPO <sub>4</sub> <sup>43,e</sup>		32' (F)	MC, t	X	
	2/ $m'$ (AF)	t	–	TbOOH, <sup>46</sup> Ba <sub>2</sub> Ni <sub>3</sub> F <sub>10</sub> <sup>37</sup>		$\bar{3}m$ (AF)	t	X	Gd <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> <sup>60</sup>
	2'/ $m$ (AF)	–	t	TbPO <sub>4</sub> <sup>47,f</sup>	$\bar{3}m'$ (AF)	–	X	Nb <sub>2</sub> Mn <sub>4</sub> O <sub>9</sub> <sup>61,g</sup>	
Rhombic	2mm (AF)	P, t	–	Ba <sub>2</sub> CoGe <sub>2</sub> O <sub>7</sub> $B_{[110]}$ <sup>27,h</sup>		$\bar{6}$ (F)	–	X	ScMnO <sub>3</sub> , LuMnO <sub>3</sub> <sup>62</sup>
	2' $m'm$ (F)	–	T, t			$\bar{6}'$ (AF)	t	–	
	2m' $m'$ (F)	–	–			6 (F)	MC, P, t	–	
	222 (AF)	–	–	6' (AF)		–	X		
	22'2' (F)	MC, t	–	Ba <sub>2</sub> CoGe <sub>2</sub> O <sub>7</sub> $B_{[100]}$ <sup>35,i</sup>		6'/ $m$ (AF)	–	X	
	mmm' (AF)	–	t	LiNiPO <sub>4</sub> <sup>55,j</sup>		6/ $m'$ (AF)	t	–	
	$m'm'm'$ (AF)	–	–			$\bar{6}m2$ (AF)	–	X	
Tetragonal	4 (F)	MC, P, t	–	chiral metamaterial <sup>56</sup>	Hexagonal	$\bar{6}m2'$ (AF)	t	–	Fe <sub>2</sub> P <sup>63</sup>
	4' (AF)	–	–	CsCoF <sub>4</sub> <sup>37</sup>		$\bar{6}m'2$ (AF)	–	–	
	$\bar{4}$ (F)	X	–			$\bar{6}m'2'$ (F)	–	X	
	$\bar{4}'$ (AF)	t	–			6mm (AF)	P, t	–	
	4/ $m'$ (AF)	t	–	6' $mm'$ (AF)		–	X		
	4'/ $m'$ (AF)	–	–	6m' $m'$ (F)		–	–		
	$\bar{4}2m$ (AF)	–	–	62(622) (AF)		–	–		
	$\bar{4}'2'm$ (AF)	t	–	6'2(6'22') (AF)		–	X		
	$\bar{4}'2m'$ (AF)	–	–	62'(62'2') (F)		MC, t	–		
	$\bar{4}2'm'$ (F)	–	–	6'/ $mm'm$ (AF)		–	X		
	4mm (AF)	P, t	–	6/ $m'mm$ (AF)		t	–		
	4' $mm'$ (AF)	–	–	6/ $m'm'm'$ (AF)		–	–		
	4m' $m'$ (F)	–	–			$\parallel$ to 3-axis			
	42(422) (AF)	–	–	Nd <sub>5</sub> Si <sub>4</sub> <sup>57</sup>		Cubic	23 (AF)	X	
	4'2(4'2'2) (AF)	–	–			$m'\bar{3}$ (AF)	X		
42'(42'2') (F)	MC, t	–	$\bar{4}3m$ (AF)		X				
4'/ $m'm'm$ (AF)	–	–	$\bar{4}'3m'$ (AF)		–				
4/ $m'mm$ (AF)	t	–	43(432) (AF)		–				
4/ $m'm'm'$ (AF)	–	–		4'3(4'32) (AF)	X				
				$m'\bar{3}m$ (AF)	X				
				$m'\bar{3}m'$ (AF)	–				

<sup>a</sup>FeGe,<sup>20</sup> MnSi<sup>21</sup>  $B_{[111]}$ ; RbFe(MoO<sub>4</sub>)<sub>2</sub><sup>58</sup>

<sup>b</sup>Co<sub>3</sub>B<sub>7</sub>O<sub>13</sub>Cl<sup>39</sup>

<sup>c</sup>BiTeI  $B_{[100]}$ <sup>41</sup>

<sup>d</sup>FeGe,<sup>20</sup> MnSi<sup>21</sup>  $B_{[110]}$

<sup>e</sup>Cu<sub>2</sub>OSeO<sub>3</sub>  $B_{[110]}$ ;<sup>19</sup> Co<sub>3</sub>TeO<sub>6</sub>;<sup>44</sup> NdFe<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>  $B_{[010]}$ <sup>45</sup>

<sup>f</sup>MnPS<sub>3</sub>;<sup>48</sup> Co<sub>3</sub>TeO<sub>6</sub> 17 K <  $T$  < 21 K<sup>44</sup>

<sup>g</sup>Nb<sub>2</sub>Co<sub>4</sub>O<sub>9</sub><sup>61</sup>

<sup>h</sup>CuB<sub>2</sub>O<sub>4</sub>  $B_{[110]}$ ;<sup>26</sup> CdS,<sup>9</sup> AlN, GaN, InN  $B_{[100]}$ ;<sup>49</sup> CaBaCo<sub>4</sub>O<sub>7</sub>;<sup>50</sup> GaFeO<sub>3</sub>;<sup>12</sup> Co<sub>3</sub>B<sub>7</sub>O<sub>13</sub>Br;<sup>51</sup> KMnFeF<sub>6</sub><sup>37</sup>

<sup>i</sup>CuB<sub>2</sub>O<sub>4</sub>;<sup>34</sup> Ca<sub>2</sub>CoSi<sub>2</sub>O<sub>7</sub>;<sup>52</sup> Cu<sub>2</sub>OSeO<sub>3</sub>  $B_{[100]}$ ; [Ru(bpy)<sub>2</sub>(ppy)][MnCr(ox)];<sup>53</sup> one-dimensional photonic crystal with three-layered unit cell<sup>54</sup>

<sup>j</sup>one-dimensional photonic crystal with four-layered unit cell<sup>54</sup>

<sup>k</sup>ScMnO<sub>3</sub>, YMnO<sub>3</sub>, ErMnO<sub>3</sub>, TmMnO<sub>3</sub>, YbMnO<sub>3</sub>, LuMnO<sub>3</sub><sup>62</sup>



Additionally to the well-known OME and MChD, we found that 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 it inequivalent. This potential directional anisotropy effect, denoted by P in Table I, has not been studied either theoretically or experimentally so far.

Please note that whenever symmetry permits directional anisotropy of either MC- or P-type, t-type directional effect can also emerge. Nevertheless, the distinction between these cases is meaningful as the physical origin of these directional effects can be different. Besides these cases we 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 I.

Except for the magnetic point group  $\bar{4}$ , all the cases of directional anisotropy listed in Table I also have validity for other processes than light propagation. Symmetry elements of these groups cannot reverse wave propagation 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, we found that  $\bar{4}$  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 magnetoelectric tensor when dipole approximation appropriately describes the light-matter interaction. The nonvanishing elements of this tensor can be identified by the symmetry analysis of the given material. For the

static magnetoelectric tensor the result of such analysis based on magnetic point groups can be found in the literature.<sup>66</sup> While the static magnetoelectric tensor can only contain time reversal odd elements, the dynamic one may have time reversal even part as well. Therefore, the symmetry dictated form of the dynamic magnetoelectric tensor needs to be included in the constitutive relations in order to solve the 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 magnetoelectric 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 I can be reproduced. Nevertheless, we think that our 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 direction-dependent optical phenomena can emerge. Besides the conventional OME and MChD 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 nonreciprocity for any transport phenomenon, particle, or wave propagation. We identified each crystallographic magnetic point group which can host directional anisotropies providing a key for the systematic investigation of candidate materials. We also propose a large collection of crystals where these effects are expected to emerge. We also anticipate that the freedom in tailoring a broad variety of magnetic metamaterials and photonic crystals will largely extend the applicability of directional optical phenomena.

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