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On the constitutive relations of linear insulating media and related magnetoelectric effects

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ABSTRACT

General symmetry considerations are used to establish the type of constitutive relations that characterize the electromagnetic response of a material with a given magnetic point group. For clarity, the constitutive relations are generalized to explicitly include two additional secondary vector fields related to the magneto- and the electro-toroidal moments. Local energy conservation, as expressed by the Poynting-Heaviside theorem, is invoked to constrain the structure of the possible material tensors. In this way, the different types of non-dissipative materials with local interactions can be classified according to the different electromagnetic effects that are allowed by their magnetic point group symmetry. The electromagnetic response of some selected materials, chosen for illustrative purposes, is briefly discussed.

1. Introduction

Maxwell's equations specify how charges and currents generate electromagnetic fields, but not how those fields influence distributions of charges and currents within a material. Therefore, a self-consistent description of electromagnetic fields in matter requires an additional set of equations to characterize the material response, the so-called medium constitutive relations.

A constitutive relation must specify how secondary material fields, as the electric displacement $\vec{D}$ and magnetic flux density $\vec{B}$, depend on electromagnetic excitations described for instance by the electric $\vec{e}$ and magnetic $\vec{h}$ fields[1]. In most practical situations, the interaction of radiation with matter is weak enough to consider a simple linear response regime. In these cases, a constitutive relation for a given material must define the specific linear dependences of the secondary fields on the electromagnetic excitations and their spatial or temporal derivatives. Historically, these relationships have been defined mostly on an empirical and trial-and-error basis (see for instance Ref. [1] and references therein), where only fragmentary symmetry considerations take a part.

The growing interest and the increasing quest for new materials or metamaterials displaying complex optical behaviour stemming from the strong magneto-electric coupling, chirality, false chirality or non-reciprocity, recommends a more integrated analysis on the possible constitutive relations and linear cross magneto-electric effects. This work aims to draw the attention to the fact that the consideration of two additional secondary fields, together with the use of Neumann's principle [2] and the requirement of local energy conservation (as expressed by the Poynting theorem [3]), suffices to establish adequate constitutive relations for any linear insulating medium, once its magnetic point group is known. Also, the corresponding form of the electromagnetic energy density, the magneto-electric effects permitted by symmetry, and the compliance of the medium with the Lorentz theorem of reciprocity [4] can also be established.

2. The different types of excitation fields

Any quantity in physics can be classified according to the way it transforms under space inversion, $\bar{1}$, and time reversal 1'. In the particular case of vector-like quantities, which define one oriented axis in space, change sign if rotated by 180°, and comply with the usual vector algebra, one can add to those operations all the proper and improper rotations about that axis. This set of operations form the group $\infty/mm1'$ (or $D'_{\infty h}$). This group has eight 1D irreducible representations (as shown in table-1 using the notation of reference [5]).

There are four different types of vector-like quantities, each of which can be labeled by one of the four irreps that are odd under 2-fold rotations around an axis perpendicular to ∞-fold. All these four types of vectors can be identified among the primary and secondary electromagnetic fields: $\nabla \times \vec{e}$, $\vec{h}$, $\nabla \times \vec{D}$, and $\vec{B}$ are G-type vectors (space even and time even), $\vec{e}$ and $\vec{D}$ are P-type vectors (space odd and time even), $\vec{h}$ and $\vec{B}$ are M-type vectors (space even and time odd), and

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[1] This definition of "primary" and "secondary" fields is, to some extent, a matter of choice or convenience, and different combination are found in literature.

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Table 1
The eight 1d-irreps of the group $\infty/mm1'$. Here, symbols 1, $\bar{1}$, 1′, and $2_\perp$ denote the operations identity, inversion, time reversal, and a 2-fold rotation around an axis perpendicular to ∞-fold. The vector-like quantities define oriented axes in space and transform under the irreducible representations that are odd under $2_\perp$. All these four types of vectors can be identified among the primary and secondary electromagnetic fields: $\nabla\times\vec{e}$, $\vec{h}$, $\nabla\times\vec{D}$, and $\vec{B}$ are G-type vectors (space even and time even), $\vec{e}$ and $\vec{D}$ are P-type vectors (space odd and time even), $\vec{h}$ and $\vec{B}$ are M-type vectors (space even and time odd), and $\nabla\times\vec{h}$ $\nabla\times\vec{B}$, $\vec{e}$ and $\vec{D}$ are T-type vectors (space odd and time odd). The four "bi-directors" ($\overleftrightarrow{N}$, C↔, L↔, and $\overleftrightarrow{F}$), which are even under $2_\perp$, transform as the four possible types of irreducible linear isotropic response functions. The corresponding limiting groups are shown in the last column. The labels of the different irreducible representations correspond to those used in Ref. [5].

		1	$\bar{1}$	1′	$2_\perp$	Limiting group
Electro-toroidal	$\vec{G}$	1	1	1	−1	$\frac{\infty}{m}1'$
Electric	$\vec{P}$	1	−1	1	−1	$\infty m1'$
Magnetic	$\vec{M}$	1	1	−1	−1	$\frac{\infty}{m}m'$
Magneto-toroidal	$\vec{T}$	1	−1	−1	−1	$\frac{\infty}{m'}m$
Neutral	$\overleftrightarrow{N}$	1	1	1	1	$\frac{\infty}{m}m1'$
Space-odd	$\overleftrightarrow{C}$	1	−1	1	1	$\infty 21'$
Time-odd	$\overleftrightarrow{L}$	1	1	−1	1	$\frac{\infty}{m}m$
Magneto-electric	$\overleftrightarrow{F}$	1	−1	−1	1	$\frac{\infty}{m'}m'$

$\nabla\times\vec{h}$, $\nabla\times\vec{B}$, $\vec{e}$ and $\vec{D}$ are T-type vectors (space odd and time odd). This means, in particular, that there are four types of electromagnetic excitations with separate irreducible symmetries. In principle, each of these types of excitation can induce different responses in a given medium [6].

The idea that there exist four types of separate electromagnetic excitations is, in fact, an old one. Drude noted, in 1900, that the observed rotation of the polarization of a plane wave in a chiral medium could be described if an additional term proportional to $\nabla\times\vec{e}$ was added to the polarization of the medium [7]. This led Born to include in 1915 a "chiral term" in the definition of the electric displacement ($\vec{D} = \varepsilon[\vec{e} + \beta(\nabla\times\vec{e})]$) [8], and Fedorov to extend such a modification also to the definition of the magnetic induction field ($\vec{B} = \mu[\vec{h} + \beta(\nabla\times\vec{h})]$) [9,10]. In this way, it became clear that the circulations of the electric or the magnetic field (or, alternatively, their time derivatives [11]) should be considered as separate excitations [12]. Also, magneto-electric effects ($\vec{D} = \varepsilon\vec{e} + \alpha\vec{h}$ or $\vec{B} = \mu\vec{h} + \alpha\vec{e}$) were established as possible [13,14].

From a thermodynamic point of view, primary and secondary fields are defined as mutually conjugate entities that can be distinguished by their intensive or extensive nature. For instance, the electric and the electric displacement fields, $\vec{e}$ and $\vec{D}$, are examples of thermodynamic conjugate quantities ($\delta W = \vec{e}\cdot d\vec{D}$ represents a thermodynamic work). Therefore, the existence of four different types of primary electromagnetic vector fields, with separate symmetries, implies the consideration of their conjugate counterparts. Let us denote the four different types of irreducible primary excitations by $\vec{e}$, $\vec{h}$, , and $\vec{t}$, and their conjugate responses by $\vec{D}$, $\vec{B}$, $\vec{G}$, and $\vec{T}$. Then, a general linear constitutive relation relating these two sets of vectors is:

$$\begin{bmatrix}\vec{D}\\ \vec{B}\\ \vec{G}\\ \vec{T}\end{bmatrix} = \begin{bmatrix}\overline{\overline{\varepsilon}} & \overline{\overline{\alpha^d}} & \overline{\overline{\beta^d}} & \overline{\overline{\gamma^d}}\\ \overline{\overline{\alpha^b}} & \overline{\overline{\mu}} & \overline{\overline{\gamma^b}} & \overline{\overline{\beta^b}}\\ \overline{\overline{\beta^g}} & \overline{\overline{\gamma^g}} & \overline{\overline{\rho}} & \overline{\overline{\alpha^g}}\\ \overline{\overline{\gamma^t}} & \overline{\overline{\beta^t}} & \overline{\overline{\alpha^t}} & \overline{\overline{\pi}}\end{bmatrix} \times \begin{bmatrix}\vec{e}\\ \vec{h}\\ \vec{g}\\ \vec{t}\end{bmatrix} \quad (1)$$

The response of the linear medium is characterized by a set of 16 second-rank tensors (or tensor densities) that transform in different ways under space inversion and time reversal. The diagonal tensors relate vectors of the same symmetry and are, therefore, even under time reversal and space inversion. In the isotropic limit, these response functions transform as the trivial representation $\overleftrightarrow{N}$ shown in table-1, whose limiting group ($\infty/mm1'$) accepts any magnetic point group as a sub-group. Therefore, these functions are always present in any magnetic crystal. For non-diagonal tensors, however, some sort of symmetry breaking is required. The α-tensors, for instance, are odd both under time reversal 1′ and space inversion $\bar{1}$, and even under $\bar{1}' = 1' * \bar{1}$. As a result, this type of response is only allowed for magnetic point groups that accept the limiting group $\infty/m'm'$ (irrep $\overleftrightarrow{F}$) as a supergroup (magneto-electric point groups). In the same way, the β-tensors (even under time reversal 1′ and odd under space inversion $\bar{1}$ and $\bar{1}'$) and the γ-tensors (even under space inversion $\bar{1}$ and odd under 1′ and $\bar{1}'$) are only possible for space-odd point groups (those that accept the $\overleftrightarrow{C}$ limiting group $\infty 21'$ as supergroup) and time-odd point groups (those that accept the $\overleftrightarrow{L}$ limiting group ∞/mm as a supergroup), respectively.

The symmetry constraints required for the onset of the different possible electromagnetic cross-effects can, therefore, be grouped into four distinct irreducible classes, each defined by the corresponding limiting group. These classes characterize the possible types of irreducible electromagnetic media: the neutral medium (no symmetry breaking), the space-odd medium (loss of $\bar{1}$ and $\bar{1}'$), the time-odd medium (loss of 1′ and $\bar{1}'$), and magneto-electric medium (loss of 1′ and $\bar{1}$).

3. The requirement of energy conservation

Tensors within a given class share the same symmetry constraints. This fact may suggest that not all tensors in that class are independent. In the case of an insulating non-dissipative medium, for example, the requirement of energy conservation forces the linear response matrix to be Hermitian. Therefore, all the individual diagonal tensors must be Hermitian, and all the non-diagonal tensors must be related in pairs by Hermitian conjugation: $\overline{\overline{\alpha^{b(t)}}} = \overline{\overline{\alpha^{d(g)}}}^\dagger$, $\overline{\overline{\beta^{b(t)}}} = \overline{\overline{\beta^{d(g)}}}^\dagger$, and $\overline{\overline{\gamma^{b(t)}}} = \overline{\overline{\gamma^{d(g)}}}^\dagger$. In this way, the number of independent tensors is reduced to ten. It is interesting to look at this matter with more detail in order to characterize the form of the electromagnetic energy density that can be ascribed to each of the four irreducible types of electromagnetic media.

Energy conservation is usually expressed in the framework of the Poynting-Heaviside theorem [3]. The conventional interpretation of this theorem rests on a number of assumptions, which are discussed with some detail for instance in [4, 15]. One of these assumptions is that the total electromagnetic energy density of any linear medium can be identified with the electrostatic energy and the magnetic energy obtained in a quasi-static approximation, even in the case of arbitrary time-varying fields. In other words, it is assumed that the time rate of change of the energy density can be entirely expressed by two terms involving only the electric and magnetic fields ($\frac{du}{dt} = \vec{e}\cdot\dot{\vec{D}} + \vec{h}\cdot\dot{\vec{B}}$). From a symmetry point of view, however, there are four primary and four secondary irreducible fields to consider. Therefore, in general, we have four separate symmetry independent contributions to the time rate of change of the energy density:

$$\frac{du}{dt} = \vec{e}\cdot\dot{\vec{D}} + \vec{h}\cdot\dot{\vec{B}} + \vec{g}\cdot\dot{\vec{G}} + \vec{t}\cdot\dot{\vec{T}} \quad (2)$$

The additional contributions are strictly dynamical (vanish for static fields) and are non-linear (involve more than one response functions), which justifies the use of the conventional approach. However, in some cases, these dynamical contributions cannot be ignored because they are responsible for the lowest order energy signatures of some linear cross-effects.

Let us illustrate this point by considering the cases of the neutral and the space-odd media. In the first case (neutral medium), only the diagonal tensors in (1) are allowed by symmetry. To be concrete, let us take $\vec{g} = \nabla \times \vec{e}$ and $\vec{t} = \nabla \times \vec{h}$ (an alternative representation would be $\vec{g} = \dot{\vec{h}}$ and $\vec{t} = \dot{\vec{e}}$). Then, by using Maxwell equations for a transparent medium, $(\nabla \times \vec{e}) = -\dot{\vec{B}}$, and $(\nabla \times \vec{h}) = \dot{\vec{D}}$, one can cast equation (2) in the form:

$$(\frac{du}{dt})_n = \vec{e}\cdot\dot{\vec{D}} + \vec{h}\cdot\dot{\vec{B}} + (\nabla\times\vec{e})\cdot\dot{\vec{G}} + (\nabla\times\vec{h})\cdot\dot{\vec{T}} =$$

$$= \vec{e}\cdot\overline{\overline{\varepsilon}}\cdot\dot{\vec{e}} + \vec{h}\cdot\overline{\overline{\mu}}\cdot\dot{\vec{h}} + \dot{\vec{h}}\cdot(\overline{\overline{\mu}}^{\dagger}\cdot\overline{\overline{\rho}}\cdot\overline{\overline{\mu}})\cdot\ddot{\vec{h}} + \dot{\vec{e}}\cdot(\overline{\overline{\varepsilon}}^{\dagger}\cdot\overline{\overline{\pi}}\cdot\overline{\overline{\varepsilon}})\cdot\ddot{\vec{e}} =$$

$$= \frac{1}{2}\frac{d}{dt}[\vec{e}\cdot\overline{\overline{\varepsilon}}\cdot\vec{e} + \vec{h}\cdot\overline{\overline{\mu}}\cdot\vec{h} + \dot{\vec{h}}\cdot(\overline{\overline{\mu}}^{\dagger}\cdot\overline{\overline{\rho}}\cdot\overline{\overline{\mu}})\cdot\dot{\vec{h}} + \dot{e}\cdot(\overline{\overline{\varepsilon}}^{\dagger}\cdot\overline{\overline{\pi}}\cdot\overline{\overline{\varepsilon}})\cdot\dot{e}]$$

Here, the last step requires that all the diagonal tensors are Hermitian. The additional dynamical contributions to the energy density (2) involve, in this case, the product of three response functions and can be discarded in a linear approximation. The conventional approach is therefore entirely justified for a neutral medium.

Let us now consider the example of the space-odd (*s-o)* medium. In this case, in addition to the diagonal tensors, we have to take into account all the non-diagonal β-tensors in (1). Then,

$$(\frac{du}{dt})_{s-o} = (\frac{du}{dt})_n + \vec{e}\cdot\overline{\overline{\beta^d}}\cdot(\nabla\times\dot{\vec{e}}) + \vec{h}\cdot\overline{\overline{\beta^b}}\cdot(\nabla\times\dot{\vec{h}}) + (\nabla\times\vec{e})\cdot\overline{\overline{\beta^g}}\cdot\dot{\vec{e}} + (\nabla\times\vec{h})\cdot\overline{\overline{\beta^t}}\cdot\dot{\vec{h}}$$

$$= (\frac{du}{dt})_n - \vec{e}\cdot\overline{\overline{\beta^d}}\cdot\ddot{\vec{B}} + \vec{h}\cdot\overline{\overline{\beta^b}}\cdot\ddot{\vec{D}} - \dot{\vec{B}}\cdot\overline{\overline{\beta^g}}\cdot\dot{\vec{e}} + \dot{\vec{D}}\cdot\overline{\overline{\beta^t}}\cdot\dot{\vec{h}}$$

$$= (\frac{du}{dt})_n - \vec{e}\cdot\overline{\overline{\beta^d}}\cdot\ddot{\vec{B}} + \vec{h}\cdot\overline{\overline{\beta^b}}\cdot\ddot{\vec{D}} - \dot{\vec{B}}\cdot\overline{\overline{\beta^g}}\cdot\dot{\vec{e}} + \dot{\vec{D}}\cdot\overline{\overline{\beta^t}}\cdot\dot{\vec{h}}$$

$$= (\frac{du}{dt})_n - [\vec{e}\cdot\overline{\overline{\beta^d}}\cdot\overline{\overline{\mu}}\cdot\ddot{\vec{h}} + \dot{\vec{h}}\cdot\overline{\overline{\mu}}^{\dagger}\cdot\overline{\overline{\beta^g}}\cdot\dot{\vec{e}}] + [\vec{h}\cdot\overline{\overline{\beta^b}}b\cdot\overline{\overline{\varepsilon}}\cdot\ddot{\vec{e}} + \dot{\vec{e}}\cdot\overline{\overline{\varepsilon}}^{\dagger}\cdot\cdot\overline{\overline{\beta^t}}\cdot\dot{\vec{h}}] -$$

$$- [\vec{e}\cdot\overline{\overline{\beta^d}}\cdot\overline{\overline{\beta^b}}\cdot\vec{D} + \ddot{\vec{D}}\cdot\overline{\overline{\beta^b}}^{\dagger}\cdot\overline{\overline{\beta^g}}\cdot\dot{\vec{e}}] - [\vec{h}\cdot\overline{\overline{\beta^b}}\cdot\overline{\overline{\beta^d}}\cdot\vec{B} + \ddot{\vec{B}}\cdot\overline{\overline{\beta^d}}^{\dagger}\cdot\overline{\overline{\beta^t}}\cdot\dot{\vec{h}}]$$

The four additional terms can be written as time derivatives of scalar functions if $\overline{\overline{\beta^d}}^{\dagger} = \overline{\overline{\beta^g}}$, and $\overline{\overline{\beta^b}}^{\dagger} = \overline{\overline{\beta^t}}$. Retaining only the terms that are linear in the β-pseudo-tensors (which are nevertheless of the second order since they involve the product of two response functions), we obtain the lowest order correction to the electromagnetic energy density that results from breaking inversion symmetry:

$$u_{s-o} = u_n + [\vec{h}\cdot\overline{\overline{\beta^b}}\cdot\overline{\overline{\varepsilon}}\cdot\dot{\vec{e}} - \vec{e}\cdot\overline{\overline{\beta^d}}\cdot\overline{\overline{\mu}}\cdot\dot{\vec{h}}] + ... \qquad (3)$$

The new energy term represents a signature of the electro-electrotoroidal $[\vec{P} = \overline{\overline{\beta}}^{d}(\nabla\times\dot{\vec{e}})]$ and the magneto-magnetotoroidal $[\vec{M} = \overline{\overline{\beta}}^{b}(\nabla\times\dot{\vec{h}})]$ effects, which are permitted in space-odd media. It resembles the Z^{000} component of the third-rank Zilch pseudo-tensor Z^{ijk} first introduced by Lipkin [16], a quantity that has been recognized as a measure of the chirality of the field [17–23]. This is not unexpected since chirality necessarily implies the existence of electro-electrotoroidal and magneto-magnetotoroidal responses (although the converse is not true: a non-chiral medium may exhibit these effects). But, the important point to stress concerns the fact $\overline{\overline{\beta^b}}$ and $\overline{\overline{\beta^d}}$ are in fact *independent* pseudo-tensors. That is, the electro-electrotoroidal and magneto-magnetotoroidal responses of a time-odd medium are independent. Interestingly, this independence is obliterated if the energy contribution of the secondary fields $\vec{G}$ and $\vec{T}$ is ignored. In such a case, the surviving lower order terms are limited to $[-\vec{e}\cdot\overline{\overline{\beta^d}}\cdot\overline{\overline{\mu}}\cdot\ddot{\vec{h}} + \vec{h}\cdot\overline{\overline{\beta^b}}\cdot\overline{\overline{\varepsilon}}\cdot\ddot{\vec{e}}]$, and can be expressed in the desired form $\frac{d}{dt}[\vec{h}\cdot\overline{\overline{\beta^b}}\cdot\overline{\overline{\varepsilon}}\cdot\dot{\vec{e}} - \vec{e}\cdot\overline{\overline{\beta^d}}\cdot\overline{\overline{\mu}}\cdot\dot{\vec{h}}]$ only if $\overline{\overline{\beta^d}}^{\dagger} = \overline{\overline{\beta^b}}$. This type of constraint, however, is not required by symmetry [2].

An entirely similar situation occurs in the case of the time-odd medium, where the tensors $\overline{\overline{\gamma^b}}$ and $\overline{\overline{\gamma^d}}$ are independent of each other, and Hermitian conjugate to $\overline{\overline{\gamma^g}}$ and $\overline{\overline{\gamma^t}}$, respectively. Here, the lowest order signature of this effect in the energy density is $[\vec{e}\,\overline{\overline{\gamma}}^{d}\overline{\overline{\varepsilon}}\,\dot{\vec{e}} - \vec{h}\,\overline{\overline{\gamma}}^{b}\overline{\overline{\gamma}}\,\dot{\vec{h}}]$. In contrast, in the case of the magneto-electric effect, the lowest order term in the energy density, $\vec{e}\,\overline{\overline{\alpha}}^{d}\vec{h}$,is entirely due to the pseudo-tensor $\overline{\overline{\alpha}}^{d} = \overline{\overline{\alpha^b}}^{\dagger}$, while the tensors $\overline{\overline{\alpha}}^{g}$ and $\overline{\overline{\alpha}}^{t}$ give rise to separate contributions of at least of the third order. In this case, the fields $\vec{G}$ and $\vec{T}$ can again be safely ignored. The results concerning both the form of the corresponding electromagnetic energy density and the constraints imposed on the medium tensors by the requirement of local energy conservation are summarized in table-2.

4. Electromagnetic ferroics and related susceptibilities

Each of the four types of electromagnetic secondary vector fields can be induced in a medium by external forces or, if allowed by the symmetry, exist spontaneously without any external action. In this latter case, the medium is said to be ferroic or, if two or more secondary fields exist simultaneously, multiferroic[3]. Figure-1 shows the relationship between the four sets of conjugate electromagnetic vector fields and the possible sets of electromagnetic cross effects described by second rank tensors (or tensor densities). Each tensor (or tensor density) linking the same nodes are related by Hermitian conjugation.

The material tensors can be decomposed into symmetric and anti-symmetric components (for instance: $\alpha_{ij} = \alpha_{ij}{}^{S} + \frac{1}{2}a\delta_{ijk}T_k$, where the superscript S identifies the symmetric component of the tensor α_{ij}, δ_{ijk} is the Levi-Civita tensor density, $\vec{T}$ is a magneto-toroidal moment, and a is some arbitrary coefficient). The anti-symmetric components must transform as one of the four vector moments and, therefore, are only present if that vector moment is allowed by the symmetry. Hence, the four diagonal tensors may have an antisymmetric component only if the phase is ferroelectrotoroidal ($\varepsilon_{ij} = \varepsilon_{ij}{}^{S} + \frac{1}{2}g\delta_{ijk}G_k$, for instance), while the non-diagonal tensors or pseudotensors may show anti-symmetric parts in ferromagnetotoroidal ($\alpha_{ij} = \alpha_{ij}{}^{S} + \frac{1}{2}a\delta_{ijk}T_k$, as seen above), ferroelectric ($\beta_{ij} = \beta_{ij}{}^{S} + \frac{1}{2}b\delta_{ijk}P_k$, or ferromagnetic ($\gamma_{ij} = \gamma_{ij}{}^{S} + \frac{1}{2}g\delta_{ijk}M_k$) phases [4]. The structure of each of these tensors or vector moments is entirely dictated by the magnetic point group of the material and can be readily found by using, for instance, the resource *MTENSOR* available in the Bilbao Crystallographic Server [25]. Table-3 lists the possible linear effects and spontaneous vector moments permitted for each of the 122 magnetic point groups.

The response of the medium becomes more complex as its symmetry is reduced. All the holohedral magnetic point groups [$m\bar{3}m1'$(32.2.119), $6/mmm1'$ (27.2.101), $\bar{3}m1'$ (19.2.69), $4/mmm1'$ (15.2.54), $m\,mm1'$ (8.2.25), $2/m1'$ (5.2.13), and $\bar{1}1'$ (2.2.4)] forbid off-diagonal tensors and force the medium to behave as neutral. Within each crystal class, specific reductions of the full symmetry can be found to induce all the non-trivial irreducible responses. For instance, in the cubic system the groups $m'\bar{3}'m'$ (32.5.122), $4'32'$ (30.3.114), and $m\bar{3}m$ (32.1.118) ensure irreducible responses of the magneto-electric, space-odd, and

[2] This restriction has been invoked, for instance, in the analysis of the bi-isotropic medium reported in Ref. [24]. Here, the corresponding scalars β^b and β^d were forced to be equal to ensure local energy conservation.

[3] The concept of *ferroic* is here used in the sense of *pyroic*, since the possibility of domain switching by an external conjugate field is not relevant for the present analysis.

[4] The existence of a spontaneous vector moment is however a necessary but not a sufficient condition for the existence of an antisymmetric part of a second rank tensor. For example, the group $mm21'$allows the existence of a spontaneous polarization but still constrains the space-odd β-tensors to be symmetric.

Table 2
Possible constitutive relations for each of the four types of irreducible electromagnetic media. Energy conservation, as expressed by the Poynting-Heaviside theorem, imposes constraints of the material tensors (third column), and on the form of the electromagnetic energy density (fourth column: only the lowest order terms are shown).

Medium	Constitutive relations	Constraints	Energy density
neutral	$\vec{D}=\bar{\bar{\varepsilon}}\vec{e}$; $\vec{B}=\bar{\bar{\mu}}\vec{h}$; $\vec{G}=\bar{\bar{\rho}}(\nabla\times\vec{e})$; $\vec{T}=\bar{\bar{\pi}}(\nabla\times\vec{h})$	$\bar{\bar{\varepsilon}}=\bar{\bar{\varepsilon}}^{\dagger}$; $\bar{\bar{\mu}}=\bar{\bar{\mu}}^{\dagger}$; $\bar{\bar{\rho}}=\bar{\bar{\rho}}^{\dagger}$; $\bar{\bar{\pi}}=\bar{\bar{\pi}}^{\dagger}$	$\frac{1}{2}[\vec{e}\cdot\bar{\bar{\varepsilon}}\cdot\vec{e}+\vec{h}\cdot\bar{\bar{\mu}}\cdot\vec{h}+...]$
Space-odd	$\vec{D}=\bar{\bar{\varepsilon}}\vec{e}+\bar{\bar{\beta}}^{d}(\nabla\times\vec{e})$; $\vec{B}=\bar{\bar{\mu}}\vec{h}+\bar{\bar{\beta}}^{b}(\nabla\times\vec{h})$; $\vec{G}=\bar{\bar{\rho}}(\nabla\times\vec{e})+\bar{\bar{\beta}}^{g}\vec{e}$; $\vec{T}=\bar{\bar{\pi}}(\nabla\times\vec{h})+\bar{\bar{\beta}}^{t}\vec{h}$	$\bar{\bar{\varepsilon}}=\bar{\bar{\varepsilon}}^{\dagger}$; $\bar{\bar{\mu}}=\bar{\bar{\mu}}^{\dagger}$; $\bar{\bar{\rho}}=\bar{\bar{\rho}}^{\dagger}$; $\bar{\bar{\pi}}=\bar{\bar{\pi}}^{\dagger}$; $\bar{\bar{\beta}}^{t}=\overline{\overline{\beta^{b}}}^{\dagger}$; $\bar{\bar{\beta}}^{g}=\overline{\overline{\beta^{d}}}^{\dagger}$	$\frac{1}{2}[\vec{e}\cdot\bar{\bar{\varepsilon}}\cdot\vec{e}+\vec{h}\cdot\bar{\bar{\mu}}\cdot\vec{h}+...]+$ $+[\vec{h}\bar{\bar{\beta}}^{b}\bar{\bar{\varepsilon}}\dot{\vec{e}}-\vec{e}\bar{\bar{\beta}}^{d}\bar{\bar{\mu}}\dot{\vec{h}}+...]$
Time-odd	$\vec{D}=\bar{\bar{\varepsilon}}\vec{e}+\bar{\bar{\gamma}}^{d}(\nabla\times\vec{h})$; $\vec{B}=\bar{\bar{\mu}}\vec{h}+\bar{\bar{\gamma}}^{b}(\nabla\times\vec{e})$; $\vec{G}=\bar{\bar{\rho}}(\nabla\times\vec{e})+\bar{\bar{\gamma}}^{g}\vec{h}$; $\vec{T}=\bar{\bar{\pi}}(\nabla\times\vec{h})+\bar{\bar{\gamma}}^{t}\vec{e}$	$\bar{\bar{\varepsilon}}=\bar{\bar{\varepsilon}}^{\dagger}$; $\bar{\bar{\mu}}=\bar{\bar{\mu}}^{\dagger}$; $\bar{\bar{\rho}}=\bar{\bar{\rho}}^{\dagger}$; $\bar{\bar{\pi}}=\bar{\bar{\pi}}^{\dagger}$; $\bar{\bar{\gamma}}^{g}=\overline{\overline{\gamma^{b}}}^{\dagger}$; $\bar{\bar{\beta}}^{t}=\overline{\overline{\beta^{d}}}^{\dagger}$	$\frac{1}{2}[\vec{e}\cdot\bar{\bar{\varepsilon}}\cdot\vec{e}+\vec{h}\cdot\bar{\bar{\mu}}\cdot\vec{h}+...]+$ $+[\vec{e}\bar{\bar{\gamma}}^{d}\bar{\bar{\varepsilon}}\dot{\vec{e}}-\vec{h}\bar{\bar{\gamma}}^{b}\bar{\bar{\mu}}\dot{\vec{h}}+...]$
magneto-electric	$\vec{D}=\bar{\bar{\varepsilon}}\vec{e}+\bar{\bar{\alpha}}^{d}\vec{h}$; $\vec{B}=\bar{\bar{\mu}}\vec{h}+\bar{\bar{\alpha}}^{b}\vec{e}$; $\vec{G}=\bar{\bar{\rho}}(\nabla\times\vec{e})+\bar{\bar{\alpha}}^{g}(\nabla\times\vec{h})$; $\vec{T}=\bar{\bar{\pi}}(\nabla\times\vec{h})+\bar{\bar{\alpha}}^{t}(\nabla\times\vec{e})$	$\bar{\bar{\varepsilon}}=\bar{\bar{\varepsilon}}^{\dagger}$; $\bar{\bar{\mu}}=\bar{\bar{\mu}}^{\dagger}$; $\bar{\bar{\rho}}=\bar{\bar{\rho}}^{\dagger}$; $\bar{\bar{\pi}}=\bar{\bar{\pi}}^{\dagger}$; $\bar{\bar{\alpha}}^{d}=\overline{\overline{\alpha^{b}}}^{\dagger}$; $\bar{\bar{\alpha}}^{t}=\overline{\overline{\alpha^{g}}}^{\dagger}$	$\frac{1}{2}[\vec{e}\cdot\bar{\bar{\varepsilon}}\cdot\vec{e}+\vec{h}\cdot\bar{\bar{\mu}}\cdot\vec{h}+...]+$ $+[\vec{e}\bar{\bar{\alpha}}^{d}\vec{h}+...]$

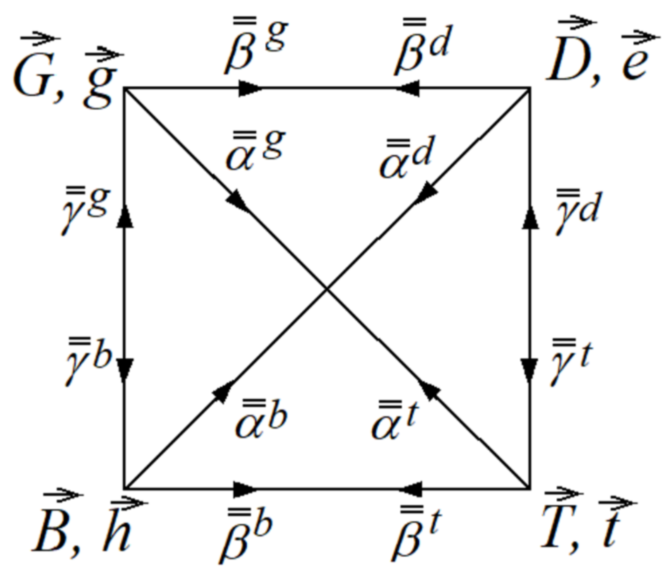

Fig. 1. The four electromagnetic ferroic orders and the related response functions. Tensors linking the same corners of the square are related by Hermitian conjugation.

time-odd type, respectively. The same happens in the triclinic system with the groups $\bar{1}'$ (2.3.5), $11'$ (1.2.2), and $\bar{1}$ (2.1.3). Further reduction of the symmetry within each class increases the complexity of the response, ensuring reducible constitutive relations for which more than one type non-diagonal tensors are allowed. For example, for the chiral cubic group 432, all the linear cross-effects are possible. This means that any of the primary excitations, by itself, is capable of inducing any of the four secondary moments. The electromagnetic response becomes especially complex in the case of seven groups [1 (1.1.1), 2 (3.1.6), $2'$ (3.3.8), m' (4.3.11) , 4 (9.1.29), 3 (16.1.60), 6 (21.1.76)] because here not only all the first order effects are allowed, but also all the four types of secondary moments can co-exist in the same system.

The structure of a given tensor for a specific magnetic point symmetry must take into account the limitations imposed by the requirement of energy conservation. For example, the diagonal tensors of any non-ferroelectrotoroidal transparent medium must be purely symmetric and, therefore, real, to preserve their Hermitic nature. In a ferroelectrotoroidal medium, these tensors may have an anti-symmetric component which, for the same reason, must be purely imaginary. Consider, for instance, the ferroelectrotoroidal group $2'/m'$(5.5.16) . Since this group allows for the existence of an electrotoroidal moment parallel to the monoclinic axis ($G_2 \neq 0$), then it also permits the existence of a purely imaginary component in any of the diagonal tensors. In the case of the dielectric tensor, for instance, the purely imaginary components $\varepsilon''_{31} = -\varepsilon''_{13} \propto iG_2$ are permitted, along with a real symmetric non-diagonal counterpart ($\varepsilon'_{31} = \varepsilon'_{13}$). Because all the non-diagonal tensors are forbidden for this symmetry, the corresponding medium remains of the neutral type: a given secondary moment is solely induced by the corresponding conjugate primary field.

The non-diagonal tensors are not constrained to be Hermitian. Consider the example of the non-pyroic and chiral group $4221'$ (12.2.41). Here, the only non-diagonal tensors allowed are the space-odd β-tensors, which are forced to be symmetric due to the non-ferroic nature of the group. Specifically, in this case, the β-tensors are constrained to be diagonal with $\beta_{11} = \beta_{22} = a$, and $\beta_{33} = b$, where a and b are complex numbers. The only constraint imposed by the Poynting-Heaviside theorem is limited to the conditions $\overline{\overline{\beta^{d}}}^{\dagger} = \overline{\overline{\beta^{g}}}$, and $\overline{\overline{\beta^{b}}}^{\dagger} = \overline{\overline{\beta^{t}}}$. In the case of a polar group, the β-tensors can also display an anti-symmetric component. This component can eventually be the only one permitted by the symmetry. In the case of the group $6mm1'$ (25.2.92), for example, the

Table-3
Electromagnetic cross-effects and ferroic phases allowed (full square ■) or forbidden (open square □) for each of the 122 magnetic point groups. Each group is denoted by its Hermann-Mauguin symbol, and by its number according to the Bilbao Server (MPOINT). Symmetry, the corresponding medium remains of the neutral type: a given secondary moment is solely induced by the corresponding conjugate primary field.

	$\bar{\bar{\alpha}}$	$\bar{\bar{\beta}}$	$\bar{\bar{\gamma}}$	$\vec{G}$	$\vec{P}$	$\vec{M}$	$\vec{T}$		$\bar{\bar{\alpha}}$	$\bar{\bar{\beta}}$	$\bar{\bar{\gamma}}$	$\vec{G}$	$\vec{P}$	$\vec{M}$	$\vec{T}$		$\bar{\bar{\alpha}}$	$\bar{\bar{\beta}}$	$\bar{\bar{\gamma}}$	$\vec{G}$	$\vec{P}$	$\vec{M}$	$\vec{T}$
1 (1.1.1)	■	■	■	■	■	■	■	4′22′ (12.3.42)	■	■	■	□	□	□	□	6/m1' (23.2.83)	□	■	□	■	□	□	□
11′ (1.2.2)	□	■	□	■	■	□	□	42′2′(12.4.43)	■	■	■	□	□	■	■	6'/m (23.3.84)	□	■	□	■	□	□	□
$\bar{1}$ (2.1.3)	□	□	■	■	□	■	□	4mm (13.1.44)	■	■	■	□	■	□	■	6/m' (23.4.85)	■	□	□	■	□	□	■
$\bar{1}$1′ (2.2.4)	□	□	□	■	□	□	□	4mm1′(13.2.45)	□	■	□	□	■	□	□	6'/m' (23.5.86)	□	□	□	■	□	□	□
$\bar{1}$′ (2.3.5)	■	□	□	■	□	□	■	4′m′m (13.3.46)	■	■	■	□	■	□	□	622 (24.1.87)	■	■	■	□	□	□	□
2 (3.1.6)	■	■	■	■	■	■	■	4m′m′ (13.4.47)	■	■	■	□	■	■	□	6221′ (24.2.88)	□	■	□	□	□	□	□
21′ (3.2.7)	□	■	□	■	■	□	□	$\bar{4}$2m (14.1.48)	■	■	■	□	□	□	□	6′22′ (24.3.89)	□	■	■	□	□	□	□
2′ (3.3.8)	■	■	■	■	■	■	■	$\bar{4}$2m1′ (14.2.49)	□	■	□	□	□	□	□	62′2′ (24.4.90)	■	■	■	□	□	■	■
m (4.1.9)	□	■	■	■	■	■	■	$\bar{4}$′2′m (14.3.50)	■	■	■	□	□	□	■	6mm (25.1.91)	■	■	■	□	■	□	■
m1′ (4.2.10)	□	■	□	■	■	□	□	$\overline{4'}$2m′ (14.4.51)	■	■	■	□	□	□	□	6mm1′(25.2.92)	□	■	□	□	■	□	□
m′ (4.3.11)	■	■	■	■	■	■	■	$\bar{4}$2′m′ (14.5.52)	■	■	■	□	□	■	□	6′mm′ (25.3.93)	□	■	□	□	■	□	□
2/m (5.1.12)	□	□	■	■	□	■	□	4/mmm (15.1.53)	□	□	■	□	□	□	□	6m′m′ (25.4.94)	■	■	■	□	■	■	□
2/m1' (5.2.13)	□	□	□	■	□	□	□	4/mmm1' (15.2.54)	□	□	□	□	□	□	□	$\bar{6}$m2 (26.1.95)	■	□	■	□	□	□	□
2'/m (5.3.14)	■	□	■	■	□	■	■	4/m'mm (15.3.55)	■	□	□	□	□	□	■	$\bar{6}$m21′ (26.2.96)	□	□	□	□	□	□	□
2/m' (5.4.15)	■	□	□	■	□	□	■	4'/mm'm (15.4.56)	□	□	■	□	□	□	□	$\bar{6}$′m′2 (26.3.97)	■	□	□	□	□	□	□
2′/m′ (5.5.16)	□	□	□	■	□	□	□	4'/m'm'm (15.5.57)	■	□	□	□	□	□	□	$\bar{6}$′m2′ (26.4.98)	■	□	□	□	□	□	■
222 (6.1.17)	■	■	■	□	□	□	□	4/mm'm' (15.6.58)	■	□	■	□	□	■	□	$\bar{6}$m′2′ (26.5.99)	□	□	■	□	□	■	□
2221′ (6.2.18)	□	■	□	□	□	□	□	4/m'm'm' (15.7.59)	■	□	□	□	□	□	□	6/mmm (27.1.100)	□	□	■	□	□	□	□
2′2′2 (6.3.19)	■	■	■	□	□	■	■	3 (16.1.60)	■	■	■	■	■	■	■	6/mmm1′ (27.2.101)	□	□	□	□	□	□	□
mm2 (7.1.20)	■	■	■	□	■	□	■	31′ (16.2.61)	□	■	□	■	■	□	□	6/m'mm (27.3.102)	■	□	□	□	□	□	■
mm21′(7.2.21)	□	■	□	□	■	□	□	$\bar{3}$ (17.1.62)	□	□	□	■	□	■	□	6'/mmm' (27.4.103)	□	□	□	□	□	□	□
m′m2′ (7.3.22)	■	■	■	□	■	■	■	$\bar{3}$1′ (17.2.63)	□	□	□	■	□	□	□	6'/m'mm' (27.5.104)	□	□	□	□	□	□	□
m′m′2 (7.4.23)	■	■	■	□	■	■	□	$\bar{3}$′ (17.3.64)	■	□	□	■	□	□	■	6/mm'm' (27.6.105)	□	□	■	□	□	■	□
mmm (8.1.24)	□	□	■	□	□	□	□	32 (18.1.65)	■	■	■	□	□	□	□	6/m'm'm' (27.7.106)	■	□	□	□	□	□	□
mmm1′(8.2.25)	□	□	□	□	□	□	□	321′ (18.2.66)	□	■	□	□	□	□	□	23 (28.1.107)	■	■	■	□	□	□	□
m′mm(8.3.26)	■	□	□	□	□	□	■	32′ (18.3.67)	■	■	■	□	□	■	■	231′ (28.2.108)	□	■	□	□	□	□	□
m′m′m (8.4.27)	□	□	■	□	□	■	□	3m (19.1.68)	■	■	■	□	■	□	■	m$\bar{3}$ (29.1.109)	■	□	■	□	□	□	□
m′m′m′(8.5.28)	■	□	□	□	□	□	□	3m1′ (19.2.69)	□	■	□	□	■	□	□	m$\bar{3}$1′ (29.2.110)	□	□	□	□	□	□	□
4 (9.1.29)	■	■	■	■	■	■	■	3m′ (19.3.70)	□	■	■	□	■	■	□	m′$\bar{3}$′ (29.3.111)	■	□	□	□	□	□	□
41′ (9.2.30)	□	■	□	■	■	□	□	$\bar{3}$m (20.1.71)	□	□	■	□	□	□	□	432 (30.1.112)	■	■	■	□	□	□	□
4′ (9.3.31)	■	■	■	■	■	□	□	$\bar{3}$m1′ (20.2.72)	□	□	□	□	□	□	□	4321′ (30.2.113)	□	■	□	□	□	□	□
$\bar{4}$ (10.1.32)	■	■	■	■	□	■	□	$\bar{3}$′m (20.3.73)	■	□	□	□	□	□	■	4′32′ (30.3.114)	□	■	□	□	□	□	□
$\bar{4}$1′ (10.2.33)	□	■	□	■	□	□	□	$\bar{3}$′m′ (20.4.74)	□	□	□	□	□	□	□	$\bar{4}$3m (31.1.115)	□	□	■	□	□	□	□
$\bar{4}$′ (10.3.34)	■	■	■	■	□	□	■	$\bar{3}$m′ (20.5.75)	■	□	■	□	□	■	□	$\bar{4}$3m1′(31.2.116)	□	□	□	□	□	□	□
4/m (11.1.35)	□	□	■	■	□	■	□	6 (21.1.76)	■	■	■	■	■	■	■	$\bar{4}$′3m′ (31.2.117)	■	□	□	□	□	□	□
4/m1′ (11.2.36)	□	□	□	■	□	□	□	61′ (21.2.77)	□	■	□	■	■	□	□	m$\bar{3}$m (32.1.118)	□	□	■	□	□	□	□
4'/m (11.3.37)	□	□	■	■	□	□	□	6′ (21.3.78)	□	■	□	■	■	□	□	m$\bar{3}$m1′(32.2.119)	□	□	□	□	□	□	□
4/m' (11.4.38)	■	□	□	■	□	□	■	$\bar{6}$ (22.1.79)	□	■	■	■	□	■	□	m′$\bar{3}$′m (32.3.120)	□	□	□	□	□	□	□
4'/m' (11.5.39)	■	□	□	■	□	□	□	$\bar{6}$1′ (22.2.80)	□	■	□	■	□	□	□	m$\bar{3}$m′ (32.4.121)	□	□	□	□	□	□	□
422 (12.1.40)	■	■	■	□	□	□	□	$\bar{6}$′ (22.3.81)	■	■	□	■	□	□	■	m′$\overline{3'}$m′(32.5.122)	■	□	□	□	□	□	□
4221′(12.2.41)	□	■	□	□	□	□	□	6/m (23.1.82)	□	■	■	■	□	■	□								

β-tensors are constrained to be purely anti-symmetry and to have a single component $\beta_{12} = -\beta_{21}$ that is proportional to a polarization along the z-axis, P_3.

As it is well known, real and imaginary components of the different constitutive tensors of a non-dissipative medium with local interactions have frequency dependences of different parity. This merely results from the fact that both primary and secondary fields are, in this case, real functions of time. In a time-odd medium, for instance, an electric polarization $\Delta\vec{P}$ can be induced by an applied toroidal magnetic field $\nabla \times \vec{h}$. In general, this linear response is non-instantaneous and can be expressed as $\Delta\vec{P}(t) = \int_{-\infty}^{t} \bar{\bar{\gamma}}(t-t')\,[\nabla \times \vec{h}(t')]\,dt'$. Here, the kernel $\bar{\bar{\gamma}}(t-t')$ is forced to be real because both $\Delta\vec{P}(t)$ and $\nabla \times \vec{h}(t')$ are real fields. As a result, its Fourier transform $\bar{\bar{\gamma}}(\omega) = \int_{-\infty}^{+\infty} \bar{\bar{\gamma}}(\tau)e^{i\omega\tau}d\tau$ is bounded to have real and imaginary components that are necessarily even and odd functions of frequency, respectively. This observation allows us to identify, in a straightforward way, which of the possible effects are or are not reciprocal.

Reciprocity can be defined in a number of ways. In network theory, for instance, a signal is called reciprocal if its propagation (in a given medium) is symmetric under the interchange of the signal source and signal detector. In the present context, it is adequate to adopt a definition that directly relates primary and secondary vector fields in linear media [26,27]. Accordingly, a given linear medium will be reciprocal if the amplitude of a secondary field, polarized along $\hat{x}_b$ and propagating along $\vec{k}_b$, arising from an exciting field of unit amplitude, polarized along $\hat{x}_a$, and with propagation vector $\vec{k}_a$, is exactly equal to the amplitude of a secondary field, polarized along $\hat{x}_a$ and propagating along $-\vec{k}_a$ that results from an exciting field of unit amplitude, polarization $\hat{x}_b$, and propagating vector $-\vec{k}_b$. With this definition, reciprocity can be traced back to the local properties of the material medium. According to Post [28], a non-dissipative medium with local interactions will be reciprocal, in the above sense, if all the elements of the constitutive tensor remain invariant under a simultaneous reversal in sign of time and frequency. With this practical definition, the reciprocal or non-reciprocal nature of a medium can be immediately checked, simply by inspecting how the symmetry allowed tensors transform under time-frequency inversion (see table-4).

The knowledge of the magnetic point group of a given material

Table 4
The reciprocal or non-reciprocal character of the effects described by the real ($\bar{\bar{x}}'$) and imaginary ($\bar{\bar{x}}''$) components of the different constitutive tensors.

Reciprocal	Non-reciprocal
$\bar{\bar{\varepsilon}}' \to \bar{\bar{\varepsilon}}'$	$\bar{\bar{\varepsilon}}'' \to \bar{\bar{\varepsilon}}''$
$\bar{\bar{\mu}}' \to \bar{\bar{\mu}}'$	$\bar{\bar{\mu}}'' \to \bar{\bar{\mu}}''$
$\bar{\bar{\rho}}' \to \bar{\bar{\rho}}'$	$\bar{\bar{\rho}}'' \to \bar{\bar{\rho}}''$
$\bar{\bar{\pi}}' \to \bar{\bar{\pi}}'$	$\bar{\bar{\pi}}'' \to \bar{\bar{\pi}}''$
$\bar{\bar{\alpha}}'' \to \bar{\bar{\alpha}}''$	$\bar{\bar{\alpha}}' \to \bar{\bar{\alpha}}'$
$\bar{\bar{\beta}}' \to \bar{\bar{\beta}}'$	$\bar{\bar{\beta}}'' \to \bar{\bar{\beta}}''$
$\bar{\bar{\gamma}}'' \to \bar{\bar{\gamma}}''$	$\bar{\bar{\gamma}}' \to \bar{\bar{\gamma}}'$
For $t \to -t$ *and* $\omega \to -\omega$	

allows us to establish both the type of the electromagnetic response and the structure of the tensors describing the linear effects permitted by the symmetry of that material. The different contributions to the electromagnetic energy density and the reciprocal or non-reciprocal character of each response function can also be readily found. The systematic use of this information provides, therefore, a rigorous and symmetry-based framework that is very useful, either in the planning of experiments or in the understanding of the different properties observed in a given material, without relying upon or invoking specific microscopic mechanisms. In the next paragraph, we explore a few practical examples to illustrate these points.

5. A few examples

5.1. Space-odd medium

The $RMnO_3$ compounds are prototype examples of the so-called "type-II magnetoelectric multiferroics" [29–33]. Let us consider the example of $TbMnO_3$ [33]. The parent phase of this compound is described by the grey group $Pbnm1'$ (z = 4). Below $T_N = 48K$, the Mn^{2+} S_y-spins form an incommensurate collinear structure modulated along the y-axis [propagation vector $\vec{k} = (0, \beta, 0)$, with $\beta \sim 0{,}27$]. The symmetry of this first incommensurate phase is described by the magnetic superspace group (mssg) $Pbnm1'(0\beta0)s00s$ [34]. At zero magnetic field and below $T_C = 27K$, the magnetic modulation acquires an additional component of modulated S_z-spins, which shares the same propagation vector but has a phase shift of $\frac{\pi}{2}$ relatively to the pre-existing S_y wave. The symmetry of this cycloidal incommensurate phase (the spins form a cycloid in the yz-plane) is described by the polar mssg $Pbn2_11'(0\beta0)s00s$ [34]. At low temperatures, a uniform magnetic field applied along the z-axis stabilizes another cycloidal phase (with the same propagation vector), this time formed by a superposition in quadrature of the original S_y-wave with a S_x-wave. The symmetry of this field induced phase is described by the polar mssg $P2_1nm1'(0\beta0)000s$. The magnetic field rotates the cycloid plane and the orientation of the spontaneous polarization changes from $\vec{P}//\hat{z}$ to $\vec{P}//\hat{x}$.

The evolution of the point group of the system across this phase sequence is $mmm1' \to mmm1' \to mm21' \to 2mm1'$ (this latter transition being induced by the magnetic field). As can be seen in table-3, the system remains neutral in the first two phases (the parent phase and the first incommensurate phase). Only the diagonal constitutive tensors are allowed, and these are forced to be symmetric (diagonal) and real. The material is therefore reciprocal. For the two cycloidal phases, the point group becomes $mm21'$,or $2mm1'$in the case of the field-induced phase. Here the material type changes from neutral to the space-odd. The complex components $\beta_{12}$and $\beta_{21}$of the β-tensors are now permitted, in addition to the diagonal tensors that remain constrained to be diagonal and real. In these phases, the system is ferroelectric but it is neither multiferroic nor magnetoelectric. Hence, it must be the presence of the

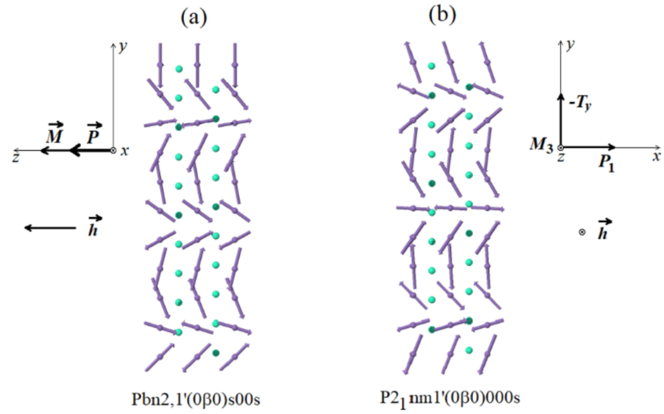

Fig. 2. The cycloidal polar phases of $TbMnO_3$: (a) In the zero field phase, the cycloid lies on the yz-plane and $\vec{P}//\hat{z}$. Here the complex components $\beta_{12}$and $\beta_{21}$of the β-tensors are allowed by symmetry and the external field $\vec{h}//\hat{z}$induces a magnetization along the z-axis (parallel to the spontaneous polarization), but cannot induce a toroidal moment; (b) For the alternative cycloid, the magnetic field induces a magnetization along the z-axis, and a magnetotoroidal moment along the y-axis (T_2) via the β^t_{23}coefficient. In this case, the sign ofT_2 can be adjusted to lower the energy of the phase via the symmetry allowed trilinear coupling $T_2M_3P_1$.

inverse magneto-magnetoroidal effect, expressed by the $\bar{\bar{\beta}}^t$,that allows an external uniform magnetic field to influence the stability of the two competing cycloidal phases. Consider the zero-field cycloidal phase (point group $mm21'$) and a magnetic field applied along the z-axis (h_3), as depicted in Fig. 2a. In this case, the external field induces a magnetization along the z-axis (parallel to the spontaneous polarization), but cannot induce a toroidal moment. For the alternative cycloid, however, $h_3$induces a magnetization along the z-axis, and a magnetotoroidal moment along the y-axis (T_2) via the β^t_{23}coefficient (see Fig. 2b). The sign ofT_2 can be adjusted to lower the energy of the phase via the symmetry allowed trilinear coupling $T_2M_3P_1$. Since $P_1 \approx (S_x^*S_y - S_y^*S_x)$, $M_3 = \mu_{33}h_3$, and $T_2 = \beta^t_{23}h_3$, the contribution of this stabilizing term grows with the square of the field and the amplitude of the S_x-wave. It is through this term that the competing cycloidal phase is stabilized by the magnetic field.

5.2. Time-odd medium

At room temperature, paramagnetic MnF_2 shows a tetragonal structure described by the grey group $P4_2/mnm1'$. Below T_N=67K, the Mn spins show an anti-ferromagnetic alignment along the z-axis, breaking time reversal and reducing the symmetry to Ref. $P4_2'/mnm'$ [35]. The point group of this magnetic phase is therefore 4'/mm'm (15.4.56), a symmetry that allows symmetric time-odd $\boldsymbol{\gamma}$-tensors with only one independent element ($\boldsymbol{\gamma}_{12} = \gamma_{21}$), and diagonal tensors constrained to be diagonal with two independent elements (for the dielectric tensor, for example, $\boldsymbol{\varepsilon}_{11} = \boldsymbol{\varepsilon}_{22} \neq \boldsymbol{\varepsilon}_{33}$). The presence of this time-odd coefficient allows several effects that can be experimentally searched for. For example, a sinusoidal electric (magnetic) field applied along the x-axis may induce an electric polarization (magnetization) along the y-axis, with the same frequency of the exciting field, due to the imaginary part of $\boldsymbol{\gamma}_{12}$. The magnitude of this effect may eventually be too small to be detected but it is certainly interesting to be aware of its existence when studying the electromagnetic response of the compound.

Similar effects can be expected for ferromagnetic $NiCr_2O_4$, but here with the addition of a spontaneous Faraday effect. This compound has a parent phase described by the paramagnetic space group $I4_1/amd1'$(point group 4/mmm1′(15.2.54)), a symmetry that forbids any non-diagonal tensors and forces a neutral response with diagonal real tensors. At $T_c = 74$K, the spins within each of the Ni and Cr sub-lattices order themselves parallel to each other, but in opposite directions $[(m_x^{Ni}, m_x^{Ni}, 0), (-m_x^{Cr}, -m_x^{Cr}, 0)]$,giving rise to a ferrimagnetic phase with a net magnetization in the xy-plane [36]. The symmetry of this ordered phase corresponds to the group $Fd'd'd$ (in a non-standard setting[5]), a symmetry that allows a spontaneous magnetization along the z-direction ([110] direction in the parent phase cell), and non-zero time-odd coefficients $\gamma_{12} \neq \gamma_{21}$.As a result, an anti-symmetric component of the γ-tensor is allowed, and a spontaneous circular birefringence is expected for light propagating along the z-axis ([110] direction in the parent phase cell).

5.3. Magnetoelectric medium

Orthorhombic $LiMnPO_4$ has a paramagnetic phase described by the grey group $Pnma1'$. At about T_N=34K the Mn spins order along the x-axis, giving rise to an antiferromagnetic phase described by the magnetic space group $Pn'm'a'$(order parameter symmetry: $m\Gamma_{1-}$) [37]. The magnetic point group changes therefore from $mmm1'$(8.2.25) to $m'm'm'$ (8.5.28), a group that forbids any ferroic order, but allows diagonal magnetoelectric, dielectric, and magnetic permeability tensors, with three independent coefficients. As a result, in the ordered phase, an electric $\vec{e}$ field applied along any crystallographic axis gives rise to a magnetization $\vec{M}$ and a polarization $\vec{P}$ parallel to that axis (via the corresponding magnetoelectric α_{ii}^b and electric susceptibility χ_{ii}^e coefficients, respectively), thus preventing the induction of a magnetotoroidal moment $\vec{T} = (\vec{P} \times \vec{M})$. But, even if the induction of a magnetotoroidal moment by an electric field via a linear effect is forbidden by the magnetic point group of the phase (see Table 2), the collinearity of the induced $\vec{M}$and $\vec{P}$ may not be kept for arbitrary orientations of the field. In that case, a magnetotoroidal moment $\vec{T}$ does arise via non-linear effects. For example, an electric field applied in the xy-plane gives rise to a magnetotoroidal moment along the z-axis, via a second-order effect ($T_3 \sim (\varepsilon_{11}\alpha_{22} - \varepsilon_{22}\alpha_{11})e_1e_2$).

It is interesting to note that a slight change in the symmetry of the order parameter may have important effects on the magnetoelectric response. Consider for instance the case of Gd_5Ge_4 (see Fig. 3). As in the preceding example, the paramagnetic phase of this compound also display the symmetry described by the magnetic space group $Pnma1'$but the magnetic ordered phase results here from the condensation of an order parameter of different symmetry ($m\Gamma_{4-}$): the three sub-lattices of Gd spins orient themselves along the z-axis, forming an antiferromagnetic arrangement with symmetry $Pnm'a$[38]. The point group changes from $mmm1'$(8.2.25) to $mm'm$(8.3.26), a magnetoelectric point group that allows two independent magnetoelectric coefficients, α_{13} and α_{31}, along with a spontaneous magnetotoroidal moment T_2. Here, an electric field applied in the xz-plane induces a magnetization that is non-collinear with the induced polarization, being the two vectors exactly orthogonal to each other when the field is oriented along the x- or z-axis. A static electric field applied along the x-axis, for instance, produces a polarization $\vec{P} \sim \varepsilon_{11}e_1\hat{x}_1$ and a magnetization $\vec{M} \sim \alpha_{31}^b e_1\hat{x}_3$. Notice that although the electric field cannot affect the magnitude or the orientation of the spontaneous magnetotoroidal moment via a linear effect (since the $\overline{\overline{\gamma}}$-tensors are null by symmetry), it can change its magnitude via a second-order effect ($\Delta T_2 \sim \alpha_{31}\varepsilon_{11}e_1^2$). Of course, these effects are maintained if the applied electric field is time dependent. But, in this case, we have also to consider the additional dynamic effect, due to $\overline{\overline{\alpha}}^g$, of the electric field induced electrotoroidal moment. For a harmonic field applied along $\vec{e}(t) = \vec{e}\cos(\omega t)\hat{x}_1$, for example, we have to consider, in addition to the induced polarization ($\vec{P} \sim \varepsilon_{11}\vec{e}\cos(\omega t)\hat{x}_1$) and magnetization $\vec{M} \sim \alpha_{31}\vec{e}\cos(\omega t)\hat{x}_3$, the induced electrotoroidal moment $\vec{G} \sim \alpha_{31}^g\omega\vec{e}\sin(\omega t)\hat{x}_3$arising from the presence of the independent magnetoelectric coefficients α_{31}^g.

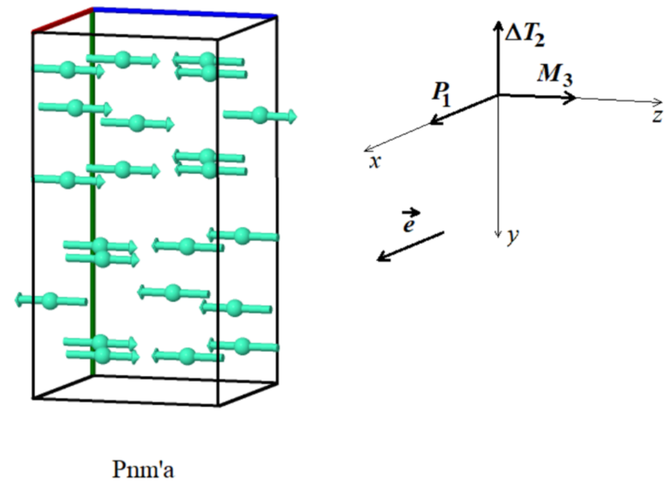

Fig. 3. The antiferromagnetic spin arrangement in Gd_5Ge_4: the magnetic point group of this magnetic phase is $mm'm$ (8.3.26), a group that permits two independent magnetoelectric coefficients, $\alpha_{13}$and α_{31}, along with a magnetotoroidal moment T_2. As a result, a static electric field applied along the x-axis (e_1) induces, via a linear effect, a polarization $\vec{P} \sim \varepsilon_{11}e_1\hat{x}_1$ and a magnetization $\vec{M} \sim \alpha_{31}^b e_1\hat{x}_3$, along with a change of the magnitude of T_2 via a second-order effect ($\Delta T_2 \sim \alpha_{31}\varepsilon_{11}e_1^2$).

5.4. Electrotoroidal neutral medium

Calcium manganese-germanium garnet, $Ca_3Mn_2Ge_3O_{12}$, has a parent cubic structure described by the space group $Pm\bar{3}m1'$. At about $T_C = 516$K there is a structural phase transition to a tetragonal phase, which originates from the cooperative ordering of the Jahn-Teller distortions of the oxygen octahedra [39–41]. The tetragonal distortion is, however, so small ($\frac{c}{a} \sim 1{,}003$) that several attempts for establishing the space group of the tetragonal phase have failed [42]. The groups $P4/mmm1'$and $P4/m1'$ have been considered as an alternative. These two groups are group-subgroup related and differ by the absence or presence of a ferroaxial distortion of symmetry Γ_{3+}(referred to the $P4/mmm1'$group). In both cases, the electromagnetic response of the material remains of the neutral type (see table-2), meaning that a given field can only excite its conjugate moment. But if that distortion exists, then a spontaneous electrotoroidal moment oriented along the tetragonal axis is allowed (G_3). Therefore, the structure of the diagonal tensors is different in the two cases: they are limited to be real and diagonal for the 4/mmm (15.11.53) point group, but have, in addition, purely imaginary non-diagonal coefficients for $4/m$(11.1.35). The dielectric tensor, for instance, is limited to two independent coefficients in the first case ($\varepsilon_{11} = \varepsilon_{22}$ and ε_{33}), and three independent coefficients in the second case ($\varepsilon_{11} = \varepsilon_{22}$, ε_{33}, and $i\varepsilon_{12} = -i\varepsilon_{21}$). Hence, a harmonic electric field applied along the x_1-axis, $\vec{e}(t) = e_1\cos(\omega t)\vec{x_1}$, gives only rise to a time-dependent polarization along that axis for $4/mmm$, but originates to an additional polarization component along the $\vec{x_2}$in the case of $4/m$. This additional component oscillates with a phase lag of $\frac{\pi}{2}$with respect to the applied electric field. This observation could eventually help to elucidate which of the two groups is actually realized in the calcium manganese-germanium garnets below their high-temperature structural transition.

5.5. Full reducible medium

At room temperature, $FePO_4$ has an orthorhombic paramagnetic structure described by the grey space group $Pnma1'$. Below$T_N = 125$K the Fe-spins order into an antiferromagnetic arrangement due to the

[5] The transformation to the standard setting is $\{(-a+b,\ c,\ a+b);\ \frac{1}{2}, 1, \frac{1}{2}\}$ [25].

condensation of a magnetic order parameter with a symmetry $m\Gamma_1$-, giving rise to a chiral phase with symmetry $P2_12_12_1$ [43]. As a result, the system changes from the neutral type (only diagonal real tensors are allowed to the full reducible type (all the material tensors are allowed). The point symmetry of the ordered phase excludes, however, all the ferroic orders, forcing all the different tensors to remain diagonal. This implies that all the cross electromagnetic effects are here permitted, and a single external field may in principle induce any type of secondary moment. For example, an electric field $e_1$applied along $\vec{x_1}$can eventually induce a polarization $[P_1 = (\frac{\varepsilon_{11}}{\varepsilon_0} - 1)e_1]$, a magnetization $[M_1 = \alpha_{11}^{b} e_1]$, a electrotoroidal moment $[G_1 = \beta_{11}^{g} e_1]$, and a magnetotoroidal moment $[T_1 = \gamma_{11}^{t} e_1]$, all parallel to that axis. For an arbitrary orientation of the field, the different induced momenta are not forced to be parallel to each other.

6. Conclusion

The constitutive relations of any linear and non-dissipative medium with local interactions can be consistently classified according to the type of electromagnetic effects that are allowed by its magnetic point group. The well-establish need to consider four different types of electromagnetic excitations with separate symmetries requires, for consistency, the explicit consideration of four conjugate secondary fields. In this way, it is ensured that all the symmetry independent contributions to the electromagnetic energy density are included, and all the constraints imposed by the conservation of energy are properly evaluated.

The type of the electromagnetic response is entirely dictated by the point symmetry. In each crystal class, the holohedral magnetic point group always forces the system to be of the neutral type. Here, the non-diagonal material tensors in (1) are forbidden, and a given excitation field can only induce its conjugate field. Appropriate reductions of symmetry within each crystal class can give rise to the onset of different irreducible responses when the particular point group accepts only one of the non-trivial limiting groups [$\infty 21'$ (space-odd), ∞/mm(time-odd), or $\infty/m'm'$(magneto-electric)] as a supergroup, Further reductions of the symmetry within each class result in partial or full reducible responses, when two or all the three limiting groups are accepted as common supergroups, respectively.

The consideration of the magnetic point group of a system provides an instrumental and often ignored information concerning the possible linear electromagnetic effects that can be expected. In this sense, symmetry offers a simple, practical and model-independent tool to interpret and explore the details of the electromagnetic response of materials

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