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Natural optical activity and its control by electric field in electrotoroidic systems

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We propose the existence, via analytical derivations, novel phenomenologies, and first-principles-based simulations, of a class of materials that are not only spontaneously optically active, but also for which the sense of rotation can be switched by an electric field applied to them via an induced transition between the dextrorotatory and laevorotatory forms. Such systems possess electric vortices that are coupled to a spontaneous electrical polarization. Furthermore, our atomistic simulations provide a deep microscopic insight into, and understanding of, this class of naturally optically active materials.

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I. INTRODUCTION

The speed of propagation of circularly polarized light traveling inside an optically active material depends on its helicity.1,2 Accordingly, the plane of polarization of linearly polarized light rotates by a fixed amount per unit length, a phenomenon known as optical rotation. One traditional way to make materials optically active is to take advantage of the Faraday effect by applying a magnetic field. However, there are some specific systems that are naturally gyrotropic, that is, they spontaneously possess optical activity. Examples of known natural gyrotropic systems are quartz,3 some organic liquids and aqueous solutions of sugar and tartaric acid,4 the PbSger2O11 compound,4,5 and the layered crystal (C3H11NH3)2ZnCl4.6 Finding novel natural gyrotropic materials has great fundamental interest. It may also lead to the design of novel devices, such as optical circulators and amplifiers, especially if the sign of the optical rotation can be efficiently controlled by an external factor that is easy to manipulate.

When searching for new natural gyrotropic materials, one should remember the observation of Pasteur that chiral crystals display spontaneous optical activity, which reverses sign when going from the original structure to its mirror image.7 Hence it is worthwhile to consider a newly discovered class of materials that are potentially chiral, and therefore may be naturally gyrotropic. This class is formed by electrotoroidic compounds (also called ferrotoroidic).8 These are systems that possess an electric toroidal moment, or equivalently, exhibit electric vortices.9 Such intriguing compounds were predicted to exist around nine years ago,10 and were found experimentally only recently.11–15 One may therefore wonder if this new class of materials is indeed naturally gyrotropic, and/or if there are other necessary conditions, in addition to the existence of an electric toroidal moment, for such materials to be optically active.

In this work, we carry out analytical derivations, original phenomenologies, and first-principles-based computations that successfully address all the aforementioned important issues. In particular, we find that electrotoroidic materials do possess spontaneous optical activity, but only if their electric toroidal moment changes linearly under an applied electric field. This linear dependence is proved to occur if the electrotoroidic materials also possess a spontaneous electrical polarization that is coupled to the electric toroidal moment, or if they are also piezoelectric with the strain affecting the value of the electric toroidal moment. We also find that, in the former case, the applied electric field further allows the control of the sign of the optical activity. Our atomistic approach also reveals the evolution of the microstructure leading to the occurrence of field-switchable gyrotropy, and it shows that the optical rotatory strength can be significant in some electrotoroidic systems.

II. RELATION BETWEEN GYROTROPY AND THE ELECTRICAL TOROIDAL MOMENT IN ELECTROTOROIDIC SYSTEMS

Let us first recall that the gyrotropy tensor elements, g_{mk}, are defined via16

\[ g_{mk} \equiv \frac{\omega}{2c} e_{ijm} \gamma_{ijk}, \tag{1} \]

where \( e_{ijm} \) is the Levi-Civita tensor,\(^{17} c \) is the speed of light, and \( \omega \) is the angular frequency. Note that this angular frequency is not restricted to the optical range. For instance, it can also correspond to the 1–100 GHz frequency range. The \( \gamma \) tensor provides the linear dependence of the dielectric permittivity on the wave vector \( \mathbf{k} \) in the optically active material, that is,\(^{16}

\[ \epsilon_{ik}(\omega,\mathbf{k}) = \epsilon_{ik}^{(0)}(\omega) + i \gamma_{ikl} k_l. \tag{2} \]

Here, \( k_l \) is the \( l \) component of the wave vector; \( \epsilon_{ik}(\omega,\mathbf{k}) \) denotes the double Fourier transform in time and space of the dielectric tensor, with the long-wavelength components being denoted by \( \epsilon_{ik}^{(0)} \). Throughout this paper we adopt Einstein notation, in which one implicitly sums over repeated indices [as it happens, e.g., for the \( l \) index in Eq. (2)]. Thus, the calculation of the gyrotropy tensor can be reduced to the calculation of the tensor \( \gamma \), which describes the spatial dispersion of the dielectric permittivity.
Alternatively, one can use the following formula for the dielectric permittivity:1,16
\[
\varepsilon_{ik}(\omega, k) = \delta_{ik} + \frac{4\pi i}{\omega} \sigma_{ikl}(\omega) = \delta_{ik} + \frac{4\pi i}{\omega} \left[ \sigma_{ikl}^{(0)}(\omega) + \sigma_{ikl}^{(0)} \right].
\] (3)

where \(\delta_{ik}\) is the Kronecker symbol and \(\sigma_{ik}(\omega, k)\) is the effective conductivity tensor in reciprocal space, at a given frequency.1 \(\sigma_{ikl}\) is the third-rank tensor associated with the linear dependence of the effective conductivity tensor on the wave vector, and \(\sigma_{ikl}^{(0)}\) is the effective conductivity tensor at zero wave vector. Combining Eq. (3) with Eq. (2) yields
\[
\gamma_{ijkl} = \frac{4\pi i}{\omega} \sigma_{ijkl}^{(0)} = \frac{4\pi i}{\omega} \left[ \sigma_{ijkl}^{(0)}(\omega) + \sigma_{ijkl}^{(0)} \right],
\] (4)

where
\[
\sigma_{ijk}^{A} = \frac{1}{2}(\sigma_{ijk} - \sigma_{jik}),
\] (5)

and
\[
\sigma_{ijkl}^{S} = \frac{1}{2}(\sigma_{ijkl} + \sigma_{jikl}).
\] (6)

Moreover, using the results of Ref. 18 and working at nonabsorbing frequencies (i.e., frequencies, such as GHz in ferroelectrics, for which the corresponding energy is below the band gap of the material), one can write
\[
\sigma_{ijk}^{A} = i\varepsilon(\varepsilon_{ijkl} - \varepsilon_{jikl}) = \omega\xi_{ijk}
\] (7)

with
\[
\beta_{ij} = i\text{Im}(\chi_{ij}^{me}) = -i\text{Im}(\chi_{ji}^{me})
\] (8)

and
\[
\xi_{ijk} = \frac{1}{2} \left[ \frac{dQ_{kj}}{dE_{i}} - \frac{dQ_{ij}}{dE_{k}} \right].
\] (9)

where Im stands for the imaginary part and \(Q\) is the quadrupole moment of the system.19 \(\chi_{ij}^{me}\) is the response of the magnetization, \(M\), to an electric field \(E\), while \(\chi_{ij}^{re}\) is the response of the electrical polarization, \(P\), to a magnetic field \(B\), that is,
\[
\chi_{ij}^{me} = \frac{dM_{i}}{dE_{j}} \quad \text{and} \quad \chi_{ij}^{re} = \frac{dP_{j}}{dB_{i}}.
\] (10)

Inserting Eq. (7) into Eq. (4) provides
\[
\gamma_{ijkl} = \frac{4\pi i}{\omega} \varepsilon(e_{ijkl}\text{Im}(\chi_{ij}^{me}) - e_{ijlk}\text{Im}(\chi_{ij}^{me})) + \omega\xi_{ijkl} + \gamma_{ijkl}^{S},
\] (11)

where \(\gamma_{ijkl}^{S} = (4\pi / \omega)\sigma_{ijkl}^{S}\) is the contribution of the symmetric part of the conductivity to the \(\gamma\) tensor. As a result, \(\gamma_{ijkl}^{S}\) is nonzero only when the system is magnetized or possesses a spontaneous magnetic order.19

Let us now focus on the magnetization, which can be written as19
\[
M = \frac{1}{2cV} \int |r \times J(r)| d^3r,
\] (12)

where \(c\) is the speed of light, \(V\) is the volume of the system, \(r\) is the position vector, and \(J(r)\) is the current density. We consider here the following contributions to this density:
\[
J(r) = \mathcal{P}(r) + c\nabla \times \mathcal{M}(r),
\] (13)

where the dot symbol indicates a partial derivative with respect to time. \(\mathcal{P}(r)\) is the polarization field, that is, the quantity for which the spatial average is the macroscopic polarization. Similarly, \(\mathcal{M}(r)\) is the magnetization field, that is, the quantity for which the spatial average is the part of the macroscopic magnetization that does not originate from the time derivative of the polarization field.20 Combining the previous two equations, we find
\[
M = \frac{1}{2cV} \int |r \times \mathcal{P}(r)| d^3r + \frac{1}{2cV} \int |r \times \nabla \times \mathcal{M}(r)| d^3r
\]
\[
= \frac{1}{2cV} \int |r \times \mathcal{P}(r)| d^3r + \mathcal{M}(r).
\] (14)

The first term in the expression on the right-hand-side bears some similarities with the definition of the electrical toroidal moment, \(G\), that is,9
\[
G = \frac{1}{2cV} \int |r \times \mathcal{P}(r)| d^3r.
\] (15)

More precisely, taking the time derivative of \(G\) gives
\[
G \simeq \frac{1}{2cV} \int |r \times \dot{\mathcal{P}}(r)| d^3r
\] (16)

when omitting the time dependency of the volume (the numerical simulations presented below indeed show that one can safely neglect this dependency when computing the time derivative of the electric toroidal moment). As a result, combining Eqs. (16) and (14) for a monochromatic wave having an \(\omega\) angular frequency gives
\[
M - \mathcal{M}(r) \simeq \frac{1}{c} \mathcal{G} = -\frac{i\omega}{c} G
\] (17)

in electrotoroidic systems.

Plugging this latter equation in Eq. (10) then gives
\[
\chi_{ij}^{me} = \chi_{ij}^{me(0)} - \frac{i\omega}{c} dG_{i} / dE_{j},
\] (18)

where \(\chi_{ij}^{me(0)}\) is the magnetoelectric tensor related to the derivative of \(\mathcal{M}(r)\) with respect to an electric field. Therefore,
\[
\text{Im}(\chi_{ij}^{me} - \chi_{ij}^{me(0)}) = -\frac{\omega}{c} dG_{i} / dE_{j}.
\] (19)

This relation between the imaginary part of the magnetoelectric susceptibility and the field derivative of the electrical toroidal moment is reminiscent of the connection discussed in Ref. 22 between the linear magnetoelectric response and the magnetic toroidal moment.

Inserting Eqs. (19) and (9) into Eq. (11) then provides
\[
\gamma_{ijkl} = \gamma_{ijkl}^{S} + \frac{4\pi c}{\omega} (e_{ijkl}\text{Im}(\chi_{ij}^{me(0)} - e_{ijlk}\text{Im}(\chi_{ij}^{me(0)}))
\]
\[
+ 4\pi \left[ e_{ijkl} dG_{ij} / dE_{k} - e_{ijlk} dG_{ij} / dE_{k} + \frac{1}{2} \left( dQ_{kj} / dE_{i} - dQ_{ij} / dE_{k} \right) \right].
\] (20)

Combining this latter equation with Eq. (1), and recalling that \(\gamma_{ijkl}^{S}\) is a symmetric tensor while \(e_{ijlm}\) is antisymmetric.
(which makes their product vanishing), gives
\[
g_{mk} = 4\pi \left( \delta_{mk} \text{Im} \frac{\partial p_{il}}{\partial E_k} \text{Im} \frac{\partial m^{(0)}_{kl}}{\partial E_l} \right) + \frac{4\pi \omega}{c} \left[ \left( \frac{dG_m}{dE_k} - \frac{dG_j}{dE_l} \right) \delta_{mk} \right] + \frac{1}{4} \delta_{ijm} \left( \frac{dQ_{ij}}{dE_l} - \frac{dQ_{kl}}{dE_j} \right). \tag{21}
\]

Choosing a specific gauge\textsuperscript{20} and neglecting quadrupole moments (simulations reported below show that spontaneous and field-induced quadrupole moments can be neglected for the ferrotoroidics numerically studied in Sec. IV) lead to the reduction of Eq. (21) to
\[
g_{mk} = \frac{4\pi \omega}{c} \left[ \left( \frac{dG_m}{dE_k} - \frac{dG_j}{dE_l} \right) \delta_{mk} \right]. \tag{22}
\]

This formula nicely reveals that optical activity should happen when the electrical toroidal moment linearly responds to an applied electric field.

III. NECESSARY CONDITIONS FOR GYROTROPY IN ELECTROTOROIDIC SYSTEMS

According to Eq. (22), an electrotoroidic system possessing nonvanishing derivatives of its electrical toroidal moment with respect to the electric field automatically possesses natural optical activity. Let us now prove analytically that the occurrence of such nonvanishing derivatives requires additional symmetry breaking in electrotoroidics, namely that an electrical polarization or/and piezoelectricity should also exist, as well as couplings between the electrical toroidal moment and electric polarization and/or strain.

For that, let us express the free energy of an electrotoroidic system having an 85% Sr composition. The nanowires have a long axis), They possess a squared cross section of $4.8 \times 4.8$ nm$^2$ in the $(x,y)$ plane, where the $x$ and $y$ axes are chosen along the pseudocubic [100] and [010] directions, respectively. The distance (along the pseudocubic [100] and [010] directions) between adjacent BaTiO$_3$ nanowires is 2.4 nm.

We choose this particular nanocomposite system because a recent theoretical study\textsuperscript{24} using an effective Hamiltonian ($H_{\text{eff}}$) scheme, revealed that its ground state possesses a spontaneous polarization along the $z$ direction inside the whole composite system, as well as electric vortices in the $(x,y)$ planes inside each BaTiO$_3$ nanowire, with the same sense of vortex rotation in every wire. Such a phase-locking, ferrotoroidic and polar state is shown in the top left panel (state 1) of Fig. 1. It exhibits an electrical toroidal moment parallel to the polarization. State 1 (the other states will be clarified

Here,
FIG. 1. (Color online) Dipole arrangement in the (x, y) plane of the studied nanocomposite for the states playing a key role in the occurrence of gyrotropy. The four wires are made of pure BaTiO$_3$, and the medium is mimicked to be formed by BST solid solutions having an 85% Sr composition. See the text for the labels and meanings of the different panels.

Below) also reveals the presence of antivortices located in the medium, half-way between the centers of adjacent vortices.

In the present study, we use the same $H_{\text{eff}}$ as in Ref. 24, combined with molecular dynamics techniques, to determine the response of this peculiar state to an ac electric field applied along the main $z$ direction of the wires. In our simulations, the amplitude of the field was fixed at $10^9$ V/m and its frequency ranged between 1 and 100 GHz. Therefore, the sinusoidal frequency-driven variation of the electric field with time makes this field range in time between $10^9$ V/m (field along [001]) and $-10^9$ V/m (field along [00-1]). The idea here is to check if the electrical toroidal moment has a linear variation with this field at these investigated frequencies, and therefore if the investigated system can possess nonzero gyrotropy coefficients [see Eq. (22)].

In this effective Hamiltonian method, developed in Ref. 25 for (Ba,Sr)TiO$_3$ (BST) compounds, the degrees of freedom are as follows: the local mode vectors in each five-atom unit cell (these local modes are directly proportional to the electric dipoles in these cells), the homogeneous strain tensor, and inhomogeneous-strain-related variables. 26 The total internal energy contains a local mode self-energy, short-range and long-range interactions between local modes, an elastic energy, and interactions between local modes and strains. Further energetic terms model the effect of the interfaces between the wires and the medium on electric dipoles and strains, as well as take into account the strain that is induced by the size difference between Ba and Sr ions and its effect on physical properties. The parameters entering the total internal energy are derived from first principles. This $H_{\text{eff}}$ can be used within
NATURAL OPTICAL ACTIVITY AND ITS CONTROL BY . . .

PHYSICAL REVIEW B 87, 195111 (2013)

for a frequency of 1 GHz at a temperature of 15 K. In practice, 
$G_z$ is computed within a lattice model\textsuperscript{24} by summing over 
the electric dipoles located at the lattice sites, rather than by 
continuously integrating the polarization field of Eq. (15) over 
the space occupied by the nanowires. The panels in Fig. 1 show 
snapshots of important states occurring during these hysteresis 
loops in order to understand gyrotropy at a microscopic level. 
A striking piece of information revealed by Fig. 2(a) is that 
$G_z$ linearly decreases with a slope of $-1.6 \, \text{e/V}$ when the 
applied ac field varies between 0 (state 1) and its maximum 
value of $10^9 \, \text{V/m}$ (state 2). Such a variation therefore results 
in positive $g_{11}$ and $g_{22}$ gyrotropy coefficients that are both 
equal to $0.94 \times 10^{-7}$ for a frequency of 1 GHz, according 
to Eq. (22) (that reduces here to $g_{11} = g_{22} = -\frac{\omega}{c} \frac{4 \pi \varepsilon_0}{\varepsilon}$ in S.I. 
units, since there are no $x$ and $y$ components of the toroidal 
moment and since the field is applied along $z$ in the studied 
case). Interestingly, we found that the aforementioned slope 
of $-1.6 \, \text{e/V}$ stays roughly constant over the entire frequency 
range we have investigated (up to 100 GHz). As a result, 
Eq. (22) indicates that $g_{11} = g_{22}$ should be proportional to 
the angular frequency $\omega$ of the applied ac field, and that the 
meaningful quantity to consider here is the ratio between 
$g_{11}$ and this frequency. Such a ratio is presently equal to 
$5.9 \times 10^{-16}$ per Hz. Moreover, the rate of optical rotation 
is related to the product between $\omega/c$ and the gyrotropy 
coefficient according to Ref. 16. As a result, the rate of 
optical rotation depends on the \textit{square} of the angular frequency 
because of Eq. (22), which is consistent with one finding of 
Biot in 1812.\textsuperscript{2} Here, the ratio of the rate of optical rotation 
to the square of the angular frequency is found to be four 
orders of magnitude larger than that measured in “typical” 
gyrotropic materials, such as Pb$_5$Ge$_3$O$_{11.45}$ As a result, the 
plane of polarization of light will rotate by around 1.2 radians 
per meter at 100 GHz (or by $1.24 \times 10^{-4}$ radians per meter at 
1 GHz) when passing through the system.

Figure 2(b) indicates that the observed decrease of $G_z$ 
is accompanied by an increase of the polarization, which is 
consistent with our numerical finding that increasing the field 
from 0 to $10^9 \, \text{V/m}$ reduces the $x$ and $y$ components of 
the electric dipoles inside the nanowires (that form the vortices) 
while enhancing the $z$ component of the electric dipoles in the 
whole nanocomposite (i.e., wires and medium). Interestingly, 
the antivortices in the medium progressively disappear during 
this linear decrease of $G_z$ and increase of $P_z$, as shown in 
Fig. 1. Figure 2 also shows that decreasing the electric field 
from $10^9 \, \text{V/m}$ (state 2) to $-0.031 \times 10^9 \, \text{V/m}$ (state 3) leads 
to a linear increase of the electric toroidal moment (yielding the 
mentioned values of $g_{11}$ and $g_{22}$), while the $z$ component 
of the polarization decreases but still stays positive.

Further increasing the magnitude of negative electric fields 
up to $\simeq -0.094 \times 10^9 \, \text{V/m}$ results in drastic changes for the 
macrostructure: dipoles in the medium now adopt a negative $z$ 
components (state 3), and sites at the interfaces between the 
medium and the wires also flip the sign of the $z$ component 
of their dipoles (states 3 and 4). During these changes, the 
overall polarization rapidly varies from a significant positive 
value along the $z$ axis to a slightly negative value [Fig. 2(b)], 
while $G_z$ is nearly constant, therefore rendering the gyrotropic 
coefficients null. Then, continually increasing the strength of 
the negative ac field up to $\simeq -0.48 \times 10^9 \, \text{V/m}$ leads to the
next stage: dipoles inside the wires begin to change the sign of their z components (states $\beta$, 4, and $\gamma$) until all of the z components of these dipoles point down (state 5). During that process, $P_z$ becomes more and more negative, while the electrical toroidal moment decreases very fast but remains positive (indicating that the chirality of the wires is unaffected by the switching of the overall polarization).

Once this process is completed, further increasing the magnitude of the applied field along [001] up to $-10^5$ V/m (state 2') leads to a linear decrease of the electrical toroidal moment. Interestingly, this decrease is quantified by a slope $dG_z/dE$ that is exactly opposite to the corresponding one when going from state 1 to state 2. As a result, the $g_{11}$ and $g_{22}$ gyroscopic coefficients associated with the evolution from state 5 to state 2' are now negative and equal to $-0.94 \times 10^{-7}$ at 1 GHz.

Finally, Figs. 1 and 2 indicate that varying now the ac field from its minimal value of $-10^0$ V/m to its maximal value of $10^6$ V/m leads to the following succession of states: 2', 5, 1', 3', $\alpha'$, $\beta'$, 4', $\gamma'$, 5', and 2, where the prime used to denote the $i'$ states (with $i = 2$, 3, 4, 5, $\alpha$, $\beta$, and $\gamma$) indicates that the corresponding states have z components of their dipoles that are all opposite to those of state 1 (for instance, state $\beta'$ has $z$ components of the dipoles being positive in the medium while being negative in the wires, which is exactly opposite to state $\beta$). During this path from state 2' to state 2, the gyroscopic coefficients $g_{11}$ and $g_{22}$ can be negative (from state 2' to state 3') or positive (from state 5' to state 2), depending on the sign of the polarization.

Such a possibility of having both negative and positive gyroscopic coefficients in the same system originates from the fact that the polarization can be down or up, and is consistent with Eqs. (31), (26), and (22). As a result, one can rotate the polarization of light either in a clockwise or anticlockwise manner in electrotoroidic systems via the control of the direction of the polarization by an external electric field—which induces the switching between the dextrorotatory and laevorotatory forms of these materials (see states 1 and 1'). Such control may be promising for the design of original devices.$^{31,35}$

Figure 3 shows how the gyrotropic coefficient $g_{11}$ depends on temperature. One can clearly see that $g_{11}$ significantly increases as the temperature increases up to 240 K. As indicated in the figure, the temperature behavior of $g_{11}$ is very well fitted by $A/\sqrt{(T_C - T)(T_G - T)}$, where $A$ is a constant, $T_C = 240$ K is the lowest temperature at which the polarization vanishes, and $T_G = 330$ K is the lowest temperature at which the electric toroidal moment is annihilated.$^{24}$ To understand such fitting, let us combine Eqs (22), (26), and (31) for the studied case, that is,

$$g_{11} = \frac{4\pi \omega}{c} \frac{dG_3}{dE_3} = -\frac{4\pi \omega}{c} \chi_{3n}^{(G)} \frac{\partial h_n^{(P)}}{\partial P} \chi_{l3}^{(P)}$$

$$= -\frac{4\pi \omega}{c} (\lambda_{nl3} + \lambda_{n3l3} + \lambda_{3nl3} + \lambda_{33l3}) \chi_{3n}^{(G)} G_3 P \chi_{l3}^{(P)}.$$  

(33)

The usual temperature dependencies of the order parameter and its conjugate field imply that $G_3$ and $P_3$ should be proportional to $\sqrt{(T_C - T)}$ and $\sqrt{(T_G - T)}$, respectively, while their responses, $\chi_{3n}^{(G)}$ and $\chi_{l3}^{(P)}$, should be proportional to $1/(T_C - T)$ and $1/(T_G - T)$, respectively. This explains why the behavior of $g_{11}$ as a function of $T$ is well described by $A/\sqrt{(T_C - T)(T_G - T)}$.

V. SUMMARY

In summary, we propose the existence of a class of spontaneously optically active materials, via the use of different techniques (namely, analytical derivations, phenomenologies, and first-principles-based simulations). These materials are electrotoroidics for which the electric toroidal moment changes linearly under an applied electric field. Such linear change is demonstrated to occur if at least one of the following two conditions is satisfied: (i) the electric toroidal moment is coupled to a spontaneous electrical polarization, or (ii) the electric toroidal moment is coupled to strain and the whole system is piezoelectric. We also report a realization of case (i) and further show that applying an electric field in such a case allows a systematic control of the sign of the optical rotation, via a field-induced transition between the dextrorotatory and laevorotatory forms. We therefore hope that our study deepens the current knowledge of natural optical activity and will be put in use to develop novel technologies.

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Note that $\mathcal{P}(r)$ and $\mathcal{M}(r)$ are technically ill-defined in the sense that they depend on the choice of a gauge. However, all the different gauges result in the same current density, $\mathcal{J}(r)$. As a result, the choice of the gauge does not modify our results in general, and Eq. (21) in particular. Such a conclusion can also be reached by realizing that the quantity appearing on the left-hand side of Eq. (12) is the macroscopic magnetization, and as such, it should not depend on the choice of a gauge. Note, however, that Eq. (22) is deduced from Eq. (21) via the annihilation of all the contributions stemming from $\mathcal{M}_0$. As a result, a specific choice of gauge was made in going from Eq. (21) to Eq. (22), namely the “P-only” gauge discussed in Ref. 21.