

Spin-orbit coupling renormalization of the natural optical activity of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ from first principlesAsier Zabalo ¹, Massimiliano Stengel ^{2,3} and Eric Bousquet ¹¹*Physique Théorique des Matériaux, Q-MAT, CESAM, Université de Liège, B-4000 Sart-Tilman, Belgium*²*Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain*³*ICREA-Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain*

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We present a first-principles study of the natural optical activity of the gyroelectric $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystal, explicitly accounting for spin-orbit coupling (SOC) effects. We derive a new analytical expression for the gyration coefficients within the recent framework of long-wavelength density-functional perturbation theory [Phys. Rev. Lett. **131**, 086902 (2023)], which significantly improves computational efficiency by reducing the number of required response functions and includes spin-orbit coupling effects. We use this implementation to investigate the evolution of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$'s optical rotation across the ferroelectric double-well, from the paraelectric $P\bar{6}$ phase to the ferroelectric $P3$ phase. Our results demonstrate that, in addition to the substantial renormalization of the double-well energy, spin-orbit coupling contributions play an equally crucial role in the natural optical activity, largely through purely electronic contributions, while SOC-induced structural relaxation effects are minor.

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I. INTRODUCTION

Lead germanate ($\text{Pb}_5\text{Ge}_3\text{O}_{11}$), referred to as PGO throughout this text, was first grown back in 1971 [1,2]. It is known to undergo a ferroelectric transition at 450 K, bringing the system from a paraelectric (PE) phase with the $P\bar{6}$ space group to a ferroelectric (FE) phase with the $P3$ space group. The latter belongs to a non-enantiomorphic Sohncke space group, which is compatible with chirality, meaning that left- and right-handed structures can crystallize in the same space group [3]. This $P\bar{6}$ to $P3$ structural phase transition has little impact on the lattice parameters of the crystal, and, in both phases, the system can be described by a primitive unit cell of 57 atoms. Since its synthesis and the experimental confirmation of a stable ferroelectric phase, it has been the subject of numerous experiments concerning its geometrical structure [4,5], ferroelectricity [6] and ferroelectric domain walls [7–9], piezoelectricity [10], dielectric response [11], and optical and electro-optical [12,13] properties. In addition to extensive experimental studies, first-principles calculations based on density functional theory (DFT) have recently been employed [6,14] to shed light on the microscopic origins of its structural phase transition, ferroelectricity, and chirality, revealing that spin-orbit coupling (SOC) effects play a critical role. One of PGO's most remarkable properties is that it can switch its natural optical activity under an applied electric field, a property also called gyroelectricity [15–17] or ferrogyrotropy [18,19]. It is also worth noting that PGO exhibits an electrogyration coefficient [12,20] that is among the largest ever recorded [reaching a value of $\gamma_{33} = (3.1 \pm 0.3) \times 10^{-11}$ m/V in Cr-doped conditions]. Even in the absence of external electric fields, it displays spontaneous natural optical activity (NOA), which describes one of the fundamental interactions between light and matter. Mathematically, natural optical activity arises in the constitutive relations as [21] the first-order

spatial dispersion of the dielectric permittivity. It primarily manifests in experiments via optical rotation (OR), which quantifies the rotation of the plane of polarization of linearly polarized light as it passes through a crystal.

Even though nowadays experimental studies [22,23] about the natural optical activity in PGO are abundant (including investigations about the sign reversal of its optical rotation [23] under an applied electric field, which stems from a change of structural handedness caused by the reversal of its polar order parameter [6]), there has been little progress from the theoretical forefront. This might be attributed to the absence, at least until quite recently, of an accurate and accessible first-principles methodology for the computation of NOA in crystals. First-principles calculations are crucial for understanding the microscopic origins of NOA and its interaction with other material characteristics, such as electronic properties or structural chirality [3]. In recent years, several complementary approaches have been developed, including numerical methods based on the long-wavelength expansion of the electromagnetic vector potential response [24,25], analytical expressions for the NOA derived within the context of multipole theory of optical spatial dispersion in crystals [26–28], and Wannier interpolation techniques [29]. Notably, fully *ab initio* implementations have only recently been developed. One such approach, formulated within the GW-Bethe-Salpeter equation (GW-BSE) framework, was recently applied to the NOA of α -quartz [30], capturing excitonic effects at significant computational expense. A more efficient alternative had previously been developed within the context of long-wave density-functional perturbation theory (DFPT), as described in Ref. [31], which is implemented in the open source ABINIT [32,33] package. Due to its accuracy and computational efficiency, the latter implementation—which completely avoids summations over empty states, does not require any numerical derivatives, and correctly treats

self-consistent field contributions to the NOA—emerges as the most compelling choice in many cases. This methodology has been successfully applied to different chiral crystals (including trigonal Se, α -SiO₂, and α -HgS) and molecules. This implementation, however, systematically neglects spin-orbit coupling effects, which might be unjustified in the presence of heavy elements like Pb or Bi, thereby compromising the method's quantitative and qualitative predictive power in these specific cases.

In this work, we present a detailed first-principles study of the natural optical activity of the Pb₅Ge₃O₁₁ crystal. We have extended the capabilities of the existing long-wave DFPT implementation for the calculation of the natural optical activity available in the ABINIT code in order to allow the treatment of spin-orbit coupling. In addition, by exploiting the inherent electromagnetic gauge freedom of the theory, as discussed in Ref. [31], we have derived a new analytical expression for the gyration coefficients. Our new implementation reduces the number of required response functions compared to the existing approach, thereby speeding up the calculation. As a relevant case, we investigate the evolution of the natural optical activity in PGO as a function of the ferroelectric distortion from the $P\bar{6}$ to the $P3$ phase, and we evaluate the influence of spin-orbit coupling effects on the NOA.

The paper is organized as follows. In Sec. II, after introducing some basic definitions, we summarize the implementation of the NOA as it is currently available in ABINIT. We then extend the formalism to incorporate spin-orbit coupling and present a new analytical expression for the NOA. The application of our implementation to the PGO crystal is presented in Sec. III. We finish the paper with the conclusions in Sec. IV.

II. FORMALISM

A. Preliminary considerations

We restrict our analysis to time-reversal symmetric insulators with broken inversion symmetry. Under such conditions, the natural optical activity [27,34,35] emerges as the only contribution to the first-order spatial dispersion of the dielectric permittivity tensor, $\epsilon_{\alpha\beta}(\omega, \mathbf{q})$, where ω is the frequency and $\mathbf{q}$ the wave vector. Expanding $\epsilon_{\alpha\beta}(\omega, \mathbf{q})$ in powers of $\mathbf{q}$, around $\mathbf{q} = \mathbf{0}$, leads to

$$\epsilon_{\alpha\beta}(\omega, \mathbf{q}) \simeq \epsilon_{\alpha\beta}(\omega, \mathbf{q} = \mathbf{0}) + iq_{\gamma} \eta_{\alpha\beta\gamma}(\omega), \quad (1)$$

where $\eta_{\alpha\beta\gamma}(\omega)$ is the natural optical activity [21], satisfying $\eta_{\alpha\beta\gamma}(\omega) = -\eta_{\beta\alpha\gamma}(\omega)$. (Summation over repeated Cartesian indices is implicitly assumed throughout the whole text.) To eliminate the redundancy in $\eta_{\alpha\beta\gamma}(\omega)$, which contains only 9 independent components out of 27, we contract it with the Levi-Civita symbol, $\varepsilon_{\gamma\delta\alpha}$, to obtain a more compact rank-2 representation. We define

$$g_{\alpha\beta}(\omega) = \frac{1}{2} \varepsilon_{\gamma\delta\alpha} \eta_{\gamma\delta\beta}(\omega), \quad (2)$$

where $g_{\alpha\beta}(\omega)$ is commonly known as the gyration tensor. Crystal symmetries restrict the form of $g_{\alpha\beta}$, making it trivially vanish in centrosymmetric crystals [35]. In particular, among the 32 crystal classes, only 18 exhibit a nonzero $g_{\alpha\beta}$ tensor as defined by Eq. (2). By focusing on crystals with threefold point-group symmetry, which includes the ferroelectric phase

of PGO, the gyration tensor takes the following form:

$$g_{\alpha\beta}(\omega) = \begin{pmatrix} g_{11}(\omega) & g_{12}(\omega) & 0 \\ -g_{12}(\omega) & g_{11}(\omega) & 0 \\ 0 & 0 & g_{33}(\omega) \end{pmatrix}, \quad (3)$$

where the optic axis is assumed to be parallel to the z Cartesian direction. Note that the symmetric (g_{33} and g_{11}) and antisymmetric (g_{12}) components of the gyration tensor are associated with different observable physical effects. The antisymmetric components $g_{12} = -g_{21}$ (corresponding to $\eta_{131} = \eta_{232} = -\eta_{311} = -\eta_{322}$) are related to longitudinal excitons [34–36] and describe longitudinal effects of NOA. For example, for a linearly polarized light along the optic axis (which is assumed to be parallel to the z Cartesian direction in our setting) propagating along the x Cartesian direction, the η_{131} component of the NOA gives rise to a longitudinal E_1 component of the electric field, since $\mathbf{E} \parallel \mathbf{q}$. On the other hand, it is well known that for an arbitrary direction of propagation, only the symmetric part of the gyration tensor contributes to optical rotation [34,35]. In particular, the optical rotatory power for light propagating parallel to the optic (trigonal) axis depends exclusively on g_{33} [37],

$$\rho(\omega) = \frac{\omega^2}{2c^2} g_{33}(\omega), \quad (4)$$

where c is the speed of light and the gyration coefficients are real, as we assume no dissipation [34]. Following Ref. [31], we focus on the zero-frequency limit, where the quantity $\bar{\rho}(\omega) = \rho(\omega)/(\hbar\omega)^2$ tends to a constant as $\omega \rightarrow 0$. Consequently,

$$\bar{\rho} = \frac{g_{33}}{2(\hbar c)^2}, \quad (5)$$

where $\hbar$ is the reduced Planck constant and

$$\bar{\rho} = \bar{\rho}(\omega \rightarrow 0), \quad g_{\alpha\beta} = g_{\alpha\beta}(\omega \rightarrow 0). \quad (6)$$

Similarly, from now on we will assume that $\eta_{\alpha\beta\gamma}$ refers to its $\omega \rightarrow 0$ limit.

B. NOA from DFPT

In this section, we recall the main equations from Ref. [31] that describe the implementation of natural optical activity as currently available in ABINIT [33,38]. The NOA tensor is recast as a third-order derivative of the total energy,

$$\eta_{\alpha\beta\gamma} = -\frac{4\pi}{\Omega} \text{Im} E_{\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}}, \quad (7)$$

where Ω is the volume of the unit cell and

$$E_{\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} = \frac{\partial}{\partial q_{\gamma}} \left(\frac{d^2 E}{d\mathcal{E}_{\alpha}^{\mathbf{q}} d\mathcal{E}_{\beta}^{\mathbf{q}}} \right) \Big|_{\mathbf{q}=\mathbf{0}}. \quad (8)$$

Here, $\mathcal{E}^{\mathbf{q}}$ represents a spatially modulated electric field as introduced in Ref. [39]. This quantity enters the Hamiltonian via the vector potential, within an electromagnetic gauge where the scalar potential vanishes and $\mathcal{E}^{\mathbf{q}} = -\partial_t \mathbf{A}^{\mathbf{q}}$. By exploiting the “ $2n+1$ ” theorem [39], the term $E_{\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}}$ in Eq. (7) can be written exclusively in terms of response functions to uniform

field perturbations as [31]

$$E_{\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} = E_{\text{elst},\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} + 2 \int_{\text{BZ}} [d^3k] E_{\mathbf{k},\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}}, \quad (9)$$

where $[d^3k] = \Omega/(2\pi)^3 d^3k$ is a shorthand notation for the Brillouin-zone (BZ) integration and

$$E_{\text{elst},\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} = \int_{\Omega} \int n^{\mathcal{E}_{\alpha}}(\mathbf{r}) K_{\gamma}(\mathbf{r}, \mathbf{r}') n^{\mathcal{E}_{\beta}}(\mathbf{r}') d^3r d^3r'. \quad (10)$$

Here, $n^{\mathcal{E}_{\alpha}}(\mathbf{r})$ is the first-order electron density response to an electric field $\mathcal{E}_{\alpha}$, and $K_{\gamma}(\mathbf{r}, \mathbf{r}')$ represents the derivative in q_{γ} of the Hartree and exchange-correlation kernel. The quantity that needs to be integrated over the BZ in Eq. (9) is given by [31]

$$E_{\mathbf{k},\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} = \chi_{\mathbf{k}}^{\mathcal{E}_{\alpha}k_{\gamma}\mathcal{E}_{\beta}} + \gamma_{\mathbf{k}}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}k_{\gamma}} + \gamma_{\mathbf{k}}^{k_{\gamma}\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} + \mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} + (\mathcal{W}_{\mathbf{k}}^{\beta,\alpha\gamma})^*. \quad (11)$$

For three generic perturbations— λ_1 , λ_2 , and λ_3 —the $\chi_{\mathbf{k}}^{\lambda_1\lambda_2\lambda_3}$ and $\gamma_{\mathbf{k}}^{\lambda_1\lambda_2\lambda_3}$ symbols introduced in the last equation are given by

$$\chi_{\mathbf{k}}^{\lambda_1\lambda_2\lambda_3} = \sum_m f_{m\mathbf{k}} \langle u_{m\mathbf{k}}^{\lambda_1} | \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_2} | u_{m\mathbf{k}}^{\lambda_3} \rangle, \quad (12a)$$

$$\gamma_{\mathbf{k}}^{\lambda_1\lambda_2\lambda_3} = - \sum_{m,n} f_{m\mathbf{k}} \langle u_{m\mathbf{k}}^{\lambda_1} | u_{n\mathbf{k}}^{\lambda_3} \rangle \langle u_{n\mathbf{k}}^{(0)} | \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_2} | u_{m\mathbf{k}}^{(0)} \rangle, \quad (12b)$$

where $f_{m\mathbf{k}}$ is the occupation function, $|u_{m\mathbf{k}}^{\lambda}\rangle$ are first-order wave functions, and $\hat{\mathcal{H}}_{\mathbf{k}}^{\lambda} = \hat{H}_{\mathbf{k}}^{\lambda} + \hat{V}^{\lambda}$. Here, $\hat{H}_{\mathbf{k}}^{\lambda}$ represents the external perturbation and $\hat{V}^{\lambda}$ is the first-order self-consistent field (SCF) potential response [40] to λ . The remaining symbol in Eq. (11), $\mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma}$, is given by

$$\mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} = \sum_m f_{m\mathbf{k}} \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | i u_{m\mathbf{k},\gamma}^{A_{\beta}} \rangle, \quad (13)$$

where $|u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}}\rangle$ is the first-order wave-function response to a uniform electric field, and $|u_{m\mathbf{k},\gamma}^{A_{\beta}}\rangle$ represents the response to a vector potential at first-order in the wave vector $\mathbf{q}$ (see the Appendix for more details). Following Ref. [31], we split the latter into a sum of symmetric ($\mathcal{S}$) and antisymmetric ($\mathcal{A}$) contributions with respect to $\beta \leftrightarrow \gamma$ exchange as

$$\mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} = \frac{1}{2} (\mathcal{S}_{\mathbf{k}}^{\alpha,\beta\gamma} + \mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma}), \quad (14)$$

where

$$\frac{1}{2} \mathcal{S}_{\mathbf{k}}^{\alpha,\beta\gamma} = \frac{i}{2} \sum_m f_{m\mathbf{k}} \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | \partial_{\beta\gamma}^2 u_{m\mathbf{k}}^{(0)} \rangle, \quad (15a)$$

$$\frac{1}{2} \mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma} = \varepsilon_{\gamma\beta\delta} \sum_m f_{m\mathbf{k}} \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | u_{m\mathbf{k}}^{B_{\delta}} \rangle, \quad (15b)$$

where $\partial_{\beta\gamma}^2 = \partial^2/\partial k_{\beta}\partial k_{\gamma}$ represents a second derivative in $\mathbf{k}$ space and $|u_{m\mathbf{k}}^{B_{\delta}}\rangle$ is the first-order wave-function response to a uniform magnetic field. The latter accounts only for the orbital part of the response, i.e., the B_{δ} field does not interact with spins (see the Appendix for more details). In all of our equations, it should be understood that the band indices m, n run only over the occupied (valence) manifold.

C. Including spins

To include the spin degrees of freedom into the formalism, we consider the following ground-state Pauli-Schrödinger Hamiltonian [41,42]:

$$H^{(0)} = \frac{\mathbf{p}^2}{2m_e} + V(\mathbf{r}) + \frac{\hbar}{4m_e} [\nabla V(\mathbf{r}) \times \mathbf{p}] \cdot \boldsymbol{\sigma}, \quad (16)$$

where $\mathbf{p}$ is the momentum operator, $V(\mathbf{r})$ is the periodic crystal potential, m_e is the electron mass, and $\boldsymbol{\sigma}$ is the Pauli vector, $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ containing the Pauli matrices. When considering the effect of an electromagnetic field described by a vector potential $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(\mathbf{q}, \omega) e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)}$, the latter equation becomes [41]

$$H = \frac{1}{2m_e} (\mathbf{p} + e\mathbf{A})^2 + V(\mathbf{r}) + \frac{\hbar}{4m_e} [\nabla V(\mathbf{r}) \times (\mathbf{p} + e\mathbf{A})] \cdot \boldsymbol{\sigma} + g_s \frac{\mu_B}{2} (\nabla \times \mathbf{A}) \cdot \boldsymbol{\sigma}, \quad (17)$$

where $-e$ is the electron charge, $\mu_B = e\hbar/2m_e$ is the Bohr magneton, and $g_s \simeq 2.0023$ is the electron spin g factor. We only keep terms linear in the vector potential, $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} + O(\mathbf{A}^2)$, where $\hat{H}^{(0)}$ is the SOC-included ground-state Hamiltonian, and

$$\hat{H}^{(1)} = \hat{H}_{\text{orb}}^{\mathbf{A}} + \hat{H}_{\text{spin}}^{\mathbf{A}}, \quad (18)$$

where $\hat{H}_{\text{orb}}^{\mathbf{A}}$ denotes the first-order Hamiltonian describing the coupling of the vector potential to the orbital degrees of freedom, as defined by Essin *et al.* [43]. The interaction between the spins and the vector potential is treated exclusively by the second term on the right-hand side of Eq. (18),

$$\hat{H}_{\text{spin}}^{A_{\alpha}} = \frac{\partial}{\partial A_{\alpha}} \left[\frac{g_s e}{2m_e} (\nabla \times \mathbf{A}) \cdot \mathbf{S} \right], \quad (19)$$

where $\mathbf{S}$ is the spin operator, $\mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma}$. Assuming Hartree atomic units ($e = \hbar = m_e = 1$) and $g_s \approx 2$ for simplicity,

$$\hat{H}_{\text{spin}}^{A_c} = i \varepsilon_{abc} q_a \hat{H}^{\mathfrak{B}_b}, \quad (20)$$

where $\hat{H}^{\mathfrak{B}_b}$ represents the first-order external perturbation associated to the spin contribution to a magnetic field, indicated with the symbol $\mathfrak{B}$,

$$\hat{H}^{\mathfrak{B}_a} = -\frac{1}{2} \hat{\sigma}_a. \quad (21)$$

In the context of the equations derived in the previous section, the spin contribution coming from Eq. (20), which is linear in the wave vector $\mathbf{q}$, is relevant only for the response to a gradient of the vector potential, appearing in the $\mathcal{A}$ terms. It is straightforward to verify that, once the spin degrees of freedom are included, we can still write

$$\frac{1}{2} \mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma} = \varepsilon_{\gamma\beta\delta} \sum_m f_{m\mathbf{k}} \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | u_{m\mathbf{k}}^{B_{\delta}} \rangle. \quad (22)$$

This shows that the $\mathcal{A}$ contribution can again be expressed as a Berry curvature in the parameter space spanned by an electric field and a magnetic field, $\mathcal{B}$. However, $\mathcal{B}$ now accounts for both spin ($\mathfrak{B}$) and orbital (B) contributions. (More details can be found in the Appendix.) It is implicitly assumed that the bras and kets represent two-component spinor wave functions and the operators are expressed in spinorial form; that is, they

are represented as 2×2 matrices (equivalently, as 4-vectors) [44].

D. Treatment of spin-orbit coupling

The only remaining task is to include spin-orbit coupling in the calculation of all the individual contributions to the NOA. This entails introducing SOC into both the ground-state calculation and the response functions. Specifically, the latter requires the first and second derivatives with respect to the wave vector $\mathbf{k}$, and the response functions to a uniform electric and magnetic field. Spin-orbit coupling is already accounted for in the calculation of ground-state properties, the first derivatives with respect to $\mathbf{k}$, the response functions to an electric field, and the spin part of the magnetic field response. Furthermore, the response function to the orbital part of a magnetic field depends solely on first derivatives with respect to $\mathbf{k}$ (see the Appendix), which makes its extension to include SOC a straightforward task. Hence, we have implemented this new option in ABINIT. This means that, among all the ingredients required for the calculation of the NOA with SOC, only the $|\partial_{\beta\gamma}^2 u_{m\mathbf{k}}^{(0)}\rangle$ wave functions appearing in the $\mathcal{S}$ terms would require additional coding effort.

While implementing this term with SOC is possible, we propose the following alternative strategy that allows us to avoid computing the $\mathcal{S}$ contributions entirely. As discussed in Ref. [31], the analytical expression for $\eta_{\alpha\beta\gamma}$ is not unique. In fact, two different definitions of $E_{\mathbf{k},\gamma}^{\mathcal{E}_\alpha\mathcal{E}_\beta}$, as it appears in Eq. (9), can yield identical gyration coefficients, provided their difference integrates to zero over the BZ. In light of this, we choose

$$\tilde{E}_{\mathbf{k},\gamma}^{\mathcal{E}_\alpha\mathcal{E}_\beta} = E_{\mathbf{k},\gamma}^{\mathcal{E}_\alpha\mathcal{E}_\beta} - \frac{1}{2}f(\mathbf{k}), \quad (23)$$

where

$$f(\mathbf{k}) = \left. \frac{\partial E_{\mathbf{k},\mathbf{q}}^{\mathcal{E}_\alpha\mathcal{E}_\beta}}{\partial k_\gamma} \right|_{\mathbf{q}=\mathbf{0}}, \quad \text{with } \int_{\text{BZ}} [d^3k]f(\mathbf{k}) = 0. \quad (24)$$

Explicitly,

$$f(\mathbf{k}) = \mathcal{X}_{\mathbf{k}}^{\mathcal{E}_\alpha\mathcal{E}_\beta k_\gamma} + \mathcal{X}_{\mathbf{k}}^{k_\gamma \mathcal{E}_\alpha \mathcal{E}_\beta} + \mathcal{X}_{\mathbf{k}}^{\mathcal{E}_\alpha k_\gamma \mathcal{E}_\beta} + \mathcal{Y}_{\mathbf{k}}^{\mathcal{E}_\alpha \mathcal{E}_\beta k_\gamma} + \mathcal{Y}_{\mathbf{k}}^{\mathcal{E}_\alpha k_\gamma \mathcal{E}_\beta} + \mathcal{S}_{\mathbf{k}}^{\alpha,\beta\gamma} + (\mathcal{S}_{\mathbf{k}}^{\beta,\alpha\gamma})^*. \quad (25)$$

According to Eq. (23), the new (tilded) expression for the $\mathbf{k}$ -dependent part of the NOA is [45]

$$\begin{aligned} \tilde{E}_{\mathbf{k},\gamma}^{\mathcal{E}_\alpha\mathcal{E}_\beta} = & \frac{1}{2} [\mathcal{X}_{\mathbf{k}}^{\mathcal{E}_\alpha k_\gamma \mathcal{E}_\beta} + \mathcal{Y}_{\mathbf{k}}^{\mathcal{E}_\alpha \mathcal{E}_\beta k_\gamma} + \mathcal{Y}_{\mathbf{k}}^{k_\gamma \mathcal{E}_\alpha \mathcal{E}_\beta} \\ & - (\mathcal{X}_{\mathbf{k}}^{\mathcal{E}_\alpha \mathcal{E}_\beta k_\gamma} + \mathcal{X}_{\mathbf{k}}^{k_\gamma \mathcal{E}_\alpha \mathcal{E}_\beta} + \mathcal{Y}_{\mathbf{k}}^{\mathcal{E}_\alpha k_\gamma \mathcal{E}_\beta}) \\ & + \mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma} + (\mathcal{A}_{\mathbf{k}}^{\beta,\alpha\gamma})^*], \end{aligned} \quad (26)$$

where the $\mathcal{S}$ contributions do not appear. In addition to treating the SOC case, this expression significantly reduces the required number of linear-response calculations. Indeed, previously the computation of the NOA involved a total of 15 response functions: 3 from derivatives with respect to $\mathbf{k}$, 3 from derivatives with respect to an electric field, 6 from second derivatives in $\mathbf{k}$, and 3 from derivatives with respect to a magnetic field. Within our new approach, only 9 re-

sponse functions are needed, as second derivatives in $\mathbf{k}$ are not required [46].

III. RESULTS

In this section, we compute the natural optical activity of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ using our new implementation. We study the evolution of the NOA as a function of the ferroelectric polar distortion, and we discuss the relevance of SOC effects, both directly, through purely electronic effects, and indirectly, via structural relaxation. In Sec. III D we focus entirely on the spin $\mathbf{B}$ -field contributions to the Berry curvature in Eq. (22).

A. Computational details

Our first-principles calculations are performed using the DFT and DFPT implementations of the ABINIT package [33,38]. We employ fully relativistic norm-conserving pseudopotentials from the PseudoDojo website [47], under the PBEsol parametrization [48] of the generalized gradient approximation (GGA). A plane-wave energy cutoff of 40 Ha is applied and the Brillouin zone is sampled using $3 \times 3 \times 3$ $\mathbf{k}$ points [6]. No significant changes on natural optical activity are observed when the $\mathbf{k}$ -point mesh is increased up to $6 \times 6 \times 6$ $\mathbf{k}$ points. Structures are relaxed to mechanical equilibrium until the forces are smaller than 10^{-6} Ha/bohr.

Further methodological considerations arise when allowing a spin-magnetization response to a magnetic field perturbation, since it requires the treatment of a spin-density matrix in the calculations (see the Appendix for more details). The DFPT routines that treat such cases in ABINIT are implemented [44] within the local density approximation (LDA) only, which is known to predict lattice constants for PGO that deviate considerably more than those obtained with the PBEsol functional [6]. In addition, considering such a spin-density matrix increases memory usage and runtime by roughly a factor of 4, making our calculations along the full distortion path (see Sec. III B) infeasible with our available computational resources. Under these circumstances, in Secs. III B and III C we decided to stick to the PBEsol functional with SOC, as it predicts lattice constants in better agreement with experiment, while acknowledging that the spin $\mathbf{B}$ -field contributions in the $\mathcal{A}$ terms of Eq. (22) are formally neglected in this setting.

The discussion of the spin magnetic field contributions is deferred to Sec. III D, where we demonstrate that, for the particular case of lead germanite, these contributions are non-negligible, although small in magnitude, and further enhance the remaining SOC effects. Therefore, the SOC-included results of Secs. III B and III C, which neglect spin- $\mathbf{B}$ contributions, provide an accurate lower-bound estimate of the total response.

B. Natural optical activity as a function of the ferroelectric distortion

To study the evolution of the NOA as a function of the ferroelectric distortion in PGO, we perform a linear interpolation, at fixed unit-cell parameters, between the high-symmetry paraelectric (PE) phase and the low-symmetry ferroelectric (FE) phase, which belong to the space group $P\bar{6}$ and $P3$,

TABLE I. Lattice parameters a and c (in Å) and unit-cell volume Ω (in Å³) of the $P\bar{6}$ phase of PGO, after full optimization of the structure, with (w) and without (wo) SOC. The last row shows the experimental values reported in Ref. [49], at 473 K.

	a	c	Ω
w SOC	10.221	10.669	965.267
wo SOC	10.214	10.682	965.083
Expt. [49]	10.260	10.696	

respectively. We start by fully relaxing the PE phase to mechanical equilibrium. The obtained optimized lattice parameters and unit-cell volume are shown in Table I. These values are in good agreement with experiments [49] and previous theoretical calculations [6]. The reference FE phase that we use to make the linear interpolation is obtained with the cell parameters fixed to those of the fully relaxed PE phase, while the ionic positions are relaxed. We define the amplitude of the global distortion as

$$d = \sqrt{\frac{1}{M} \sum_{\kappa} m_{\kappa} |\mathbf{u}_{\kappa}|^2}, \quad (27)$$

where m_{κ} is the mass of atom κ , $M = \sum_{\kappa} m_{\kappa}$ is the total mass of the unit cell, and $\mathbf{u}_{\kappa}$ denotes the displacement of atom κ from its position in the PE reference structure to its position in the FE phase.

To assess the impact of spin-orbit coupling, we study three cases: (i) the case where SOC is completely neglected, (ii) the case where SOC is fully taken into account, including SOC-induced structural relaxation effects, and (iii) a case where the calculations are done without SOC, but with a structure frozen to the one obtained with SOC. The latter will enable us to account for SOC effects coming from the electrons only. This is of special relevance in the context of natural optical activity, where the structural parameters have been shown to significantly alter the final result on their own [31].

As a first step, we show in Fig. 1 the evolution of the energy as a function of the amplitude of the global distortion d , as defined in Eq. (27). When SOC is taken into account for both the structural relaxation and the energy calculation (red bullets in Fig. 1), we obtain a double-well depth of $\Delta E = -80$ meV at a distortion amplitude $d = 0.129$ Å. The double-well energy depth is substantially reduced to $\Delta E = -61$ meV when SOC is not taken into account, neither during the relaxation nor in the energy calculation (blue squares in Fig. 1), which is in agreement with previous works [6]. In this case, the minimum energy is achieved at a distortion amplitude of $d = 0.122$ Å. Within the frozen SOC-optimized structure but removing SOC in the computation of the energy yields $\Delta E = -60$ meV (data in gray in Fig. 1). This value is very close to the case where the structure is relaxed without SOC, suggesting that the SOC-driven relaxation of the atomic positions plays only a minor role in the resulting double-well depth. These substantial SOC effects on the potential energy landscape of lead germanate have been previously discussed in Ref. [14].

Next, by means of our new NOA implementation introduced in Sec. II C, we compute the evolution of the gyration

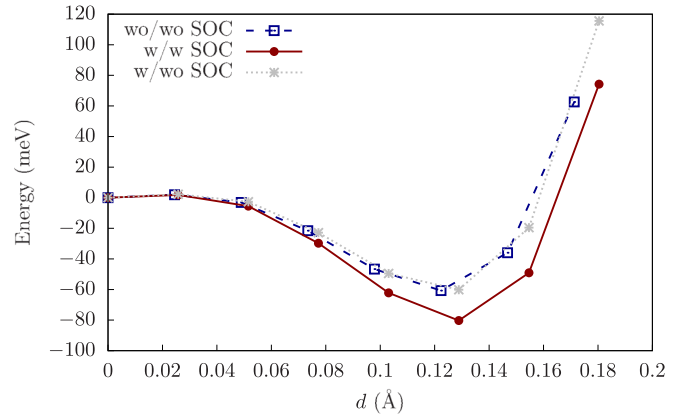


FIG. 1. Evolution of the energy as a function of the FE distortion connecting the $P\bar{6}$ (at zero distortion) and $P3$ phases, where the reference energy corresponds to that of the PE phase. The notation “w/wo SOC” indicates whether SOC is included in the structure relaxation (“w” for with, “wo” for without) and in the subsequent DFT and DFPT calculations (e.g., energy or NOA). For example, “w/wo SOC” means that the structure was relaxed with SOC, but calculations are performed without SOC. Solid and dashed lines are a guide to the eye.

coefficients as a function of the FE distortion. As shown in Fig. 2, each gyration component exhibits a different trend with increasing distortion. The absolute value of g_{33} increases more rapidly than that of g_{12} for small distortions. However, this behavior reverses for larger values of d , where $|g_{12}|$ becomes larger than $|g_{33}|$ at roughly $d \sim 0.145$ Å and $d \sim 0.14$ Å, for the w/w SOC and wo/wo SOC cases, respectively. The physical reason of this behavior is difficult to identify in view of the complexity of the PGO structure and the FE distortions.

On the other hand, the g_{11} component is small in magnitude and shows little variation across the whole distortion range. In spite of that, we observe an interesting behavior: it is positive up to a distortion of roughly $d \sim 0.1$ Å, after which it becomes

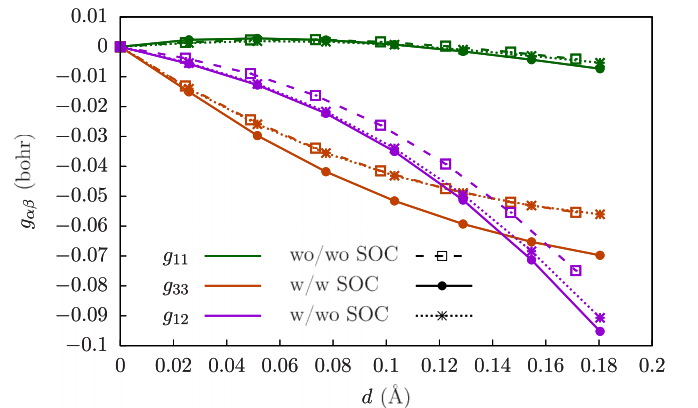


FIG. 2. Evolution of the independent components of the gyration tensor (g_{11} , g_{12} , and g_{33}) as a function of the FE distortion connecting the $P\bar{6}$ (at zero distortion) and $P3$ phases. Each individual component of the gyration tensor is represented with a different color, whereas the line style indicates whether SOC is included or not. See the caption of Fig. 1 for the definition of the shorthand notation used throughout this work. Solid and dashed lines are a guide to the eye.

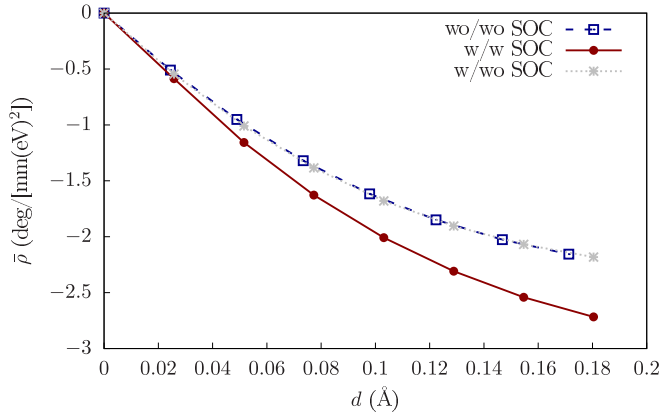


FIG. 3. Evolution of the optical rotatory power of PGO as a function of the FE distortion connecting the $P\bar{6}$ (at zero distortion) and $P3$ phases. See the caption of Fig. 1 for the definition of the shorthand notation used throughout this work. Solid and dashed lines are a guide to the eye.

negative. Recall that the distortion path under consideration does not correspond to the system’s minimum energy path, as we are linearly interpolating between the initial (PE) and final (FE) configurations. As a consequence, the observed sign reversal might be an artifact of the chosen path, instead of a physically meaningful phenomenon.

Looking now at the impact of SOC on the gyration coefficients, we observe significant effects on both g_{12} and g_{33} . Overall, the inclusion of SOC amplifies the absolute value of all the gyration components. Both structural and purely electronic contributions appear to play a comparable role in determining the final numerical value of g_{12} . In contrast, our results indicate that the SOC-induced contributions in g_{33} arise predominantly from purely electronic effects. This can be clearly deduced from Fig. 2, where the solid line (w/w SOC) and the dotted pattern line (w/wo SOC) are obtained with the same structure, and differ only from the fact that SOC has been activated or deactivated for the NOA calculation. The conclusions drawn for g_{33} can be straightforwardly extended to the optical rotatory power, as defined by Eq. (5).

We show in Fig. 3 the optical rotatory power of PGO (in units of $\text{deg}/[\text{mm}(\text{eV})^2]$) as a function of the FE distortion. Unless SOC is explicitly included into the calculation of the NOA, we can see that the SOC-induced relaxation effects have little impact on the optical rotatory power. Actually, when SOC is disabled in the NOA calculation, we obtain nearly identical results regardless of whether the structures used for interpolation are relaxed with or without SOC, which correspond, respectively, to the gray and blue data in Fig. 3. This suggests that the renormalization of atomic positions due to SOC plays only a minor role in determining the magnitude of the optical rotation, and it indicates that the effect is primarily electronic in origin.

To shed light on the microscopic origin of this effect, we analyze the SOC-induced changes in the electronic structure, focusing in particular on their impact on the electronic band gap at Γ , E_g . We note that the reduction of E_g is dominated by the inclusion of SOC in the electronic structure rather than by SOC-induced atomic relaxation

TABLE II. Lattice parameters (in Å) and unit-cell volume (in Å³) of the $P3$ phase of PGO and energy difference (in meV) with respect to the reference $P\bar{6}$ phase. P_z represents the projection of the spontaneous polarization (in $\mu\text{C}/\text{cm}^2$) along the z Cartesian direction, parallel with the trigonal C_3 rotation axis. The “full” label indicates relaxation of both cell parameters and ionic positions.

	a	c	Ω	ΔE	P_z
w SOC (full)	10.257	10.689	973.900	−89	5.5
wo SOC (full)	10.245	10.698	972.542	−68	4.6
Exp.	10.251 ^a	10.685 ^a			5.0 ^b

^aReference [51].

^bReference [50].

effects. In particular, at the energy minimum along the distortion path of Fig. 1, the calculated band-gap values at Γ and optical rotatory powers are $E_g = 2.24 \text{ eV}$ and $\bar{\rho} = -2.31 \text{ deg}/[\text{mm}(\text{eV})^2]$ for the w/w SOC case, $E_g = 2.49 \text{ eV}$ and $\bar{\rho} = -1.90 \text{ deg}/[\text{mm}(\text{eV})^2]$ for the w/wo SOC case, and $E_g = 2.47 \text{ eV}$ and $\bar{\rho} = -1.85 \text{ deg}/[\text{mm}(\text{eV})^2]$ for the wo/w/o SOC case. Since the NOA scales approximately as E_g^{-2} , this SOC-induced band-gap reduction accounts for a substantial part of the differences among the three cases. Indeed, the enhancement expected from the E_g^{-2} scaling is close to that observed in the calculated optical rotatory powers. Nevertheless, the optical rotation also depends on the relevant optical transition matrix elements, which are themselves modified by SOC. Therefore, the quantitative SOC enhancement cannot be understood solely in terms of the band-gap reduction, although this appears to provide the leading contribution to the effect.

C. Effect of full relaxation

In this section, we present the calculated values for the independent components of the gyration tensor for the fully relaxed $P3$ phase of PGO, both with and without SOC. By directly comparing these results with those from the previous section, where the study was conducted at fixed cell parameters of the $P\bar{6}$ phase, we can evaluate the impact of full cell relaxation on the NOA. The structural details and the energy difference with respect to the reference $P\bar{6}$ phase, denoted by ΔE , are reported in Table II. The computed spontaneous polarization along the hexagonal c -axis agrees well with the experimental low-temperature saturation value of Ref. [50].

For a meaningful comparison with the quantities of Sec. III B, we consider the cases at the local minima of the double-well potential in Fig. 1, corresponding to $d = 0.129 \text{ Å}$ for w/w SOC and w/wo SOC cases, and $d = 0.122 \text{ Å}$ for the wo/w/o SOC case. We provide in Table III the relevant $g_{\alpha\beta}$ tensor entries and the optical rotatory power for different cases under study. The data in Table III are gathered into pairs, so that the comparison between the fully relaxed cases and the results at fixed cell parameters of Sec. III B is easier. These values indicate that the effect of the full cell relaxation on g_{33} is minimal, though larger deviations are observed for g_{12} and g_{11} . In particular, the deviations of “w/w SOC” and “wo/w/o SOC (full)” cases with respect to the reference “w/w SOC (full)” case are 2% and 21%, respectively, for the optical

TABLE III. Independent components of the $g_{\alpha\beta}$ tensor (in bohr and optical rotatory power (in deg/[mm(eV)²]) of the $P3$ phase of PGO, for different cases. See the caption of Fig. 1 for the definition of the shorthand notation used throughout this work.

	g_{11}	g_{12}	g_{33}	$\bar{\rho}$
w/w SOC (full)	-0.0006	-0.0601	-0.0607	-2.36
w/w SOC	-0.0015	-0.0513	-0.0593	-2.31
wo/wo SOC (full)	0.0005	-0.0457	-0.0480	-1.87
wo/wo SOC	0.0002	-0.0392	-0.0475	-1.85
w/wo SOC (full)	-0.0002	-0.0576	-0.0496	-1.93
w/wo SOC	-0.0010	-0.0495	-0.0489	-1.90

rotatory power. The optical rotation in the “w/wo SOC (full)” case, which provides insight into the purely electronic SOC effects, shows a deviation of 18%, further supporting the conclusion drawn in the previous section that SOC contributions to the optical rotatory power in PGO are predominantly electronic in nature.

We also note that g_{11} is negative (positive) whenever the structure relaxation is performed with (without) SOC, irrespective of whether spin-orbit coupling is included in the subsequent calculations for the NOA. Nonetheless, its absolute value is two orders of magnitude smaller than that of g_{12} and g_{33} in nearly all cases.

D. Spin $\mathbf{B}$ -field contributions

With the goal of capturing the spin contributions to the $\mathcal{A}$ terms in Eq. (22) coming from a $\mathbf{B}$ -field response, here we present calculations using fully relativistic pseudopotentials under the Perdew-Wang [52] LDA exchange-correlation (XC) functional for two representative crystal structures of PGO: the experimental structure at 293 K [53] and the fully relaxed PBEsol structure from the previous subsection, which we treat as a $T = 0$ K approximation.

We show in Table IV the obtained numerical results for both structures under different computational settings. In particular, we use either LDA or PBEsol XC functionals, include or neglect SOC in the calculations, and consider or omit the

TABLE IV. Optical rotatory power (in deg/[mm(eV)²]) of the $P3$ phase of PGO for the experimental structure [4] at $T = 293$ K, and the fully relaxed PBEsol structure ($T \sim 0$ K), for different computational settings: SOC including spin- $\mathbf{B}$ contributions (SOC with spin- $\mathbf{B}$) or excluding them (SOC without spin- $\mathbf{B}$) in Eq. (22), and calculations without SOC (no SOC), using either LDA or PBEsol XC functionals.

	$T \sim 0$ K		$T = 293$ K	
	PBEsol	LDA	PBEsol	LDA
SOC with spin- $\mathbf{B}$	...	-2.48	...	-1.86
SOC without spin- $\mathbf{B}$	-2.36	-2.42	-1.74	-1.81
no SOC	-1.93	-1.95	-1.39	-1.40
Exp.	-2.6 ^a , -2.3 ^b		-1.45 ^a , -1.43 ^b	

^aReference [53].

^bReference [55].

spin $\mathbf{B}$ -field contributions when doing calculations under the LDA [54].

For a given structure, and within the same level of approximation, we see very good agreement between our PBEsol and LDA values for the optical rotatory power, suggesting that the results depend marginally on the choice of the XC functional, consistent with previous reports [31]. The spin $\mathbf{B}$ -field contributions to the optical rotatory power of lead germanate amplify the rest of spin-orbit coupling effects, though their effect is small compared to the total SOC-induced contributions. Such weak SOC-induced spin contributions are not unique to this system and have also been discussed, e.g., in the context of the kinetic magnetoelectric effect (KME) in Ref. [56]. Magnetic materials are expected to exhibit larger contributions to the optical rotatory power from these spin- $\mathbf{B}$ terms. This enhancement is expected to arise both directly, via the coupling of the external spin- $\mathbf{B}$ perturbation through the Pauli matrices on the right-hand side of the Sternheimer equation, and indirectly, through SCF effects induced by both the spin and orbital contributions to the $\mathbf{B}$ -field response (see the Appendix for details).

For the structure relaxed within PBEsol ($T \sim 0$ K), the inclusion of spin-orbit coupling is essential to obtain good agreement with experimental data extrapolated to $T = 0$ K. In contrast, for calculations based on the experimental structure at $T = 293$ K, we find, somewhat unexpectedly, that neglecting SOC leads to closer agreement with experiments. We note that the experimental lattice parameters and internal coordinates reported by Iwata *et al.* [5,53] show small but non-negligible deviations from the more recent structural measurements of Ref. [4], which we use as the reference structure for the $T = 293$ K calculations. Given that natural optical activity is known to be sensitive to even small structural details, these structural differences may partly explain the larger deviations observed when spin-orbit coupling is included in our calculations, which are otherwise expected to provide a more accurate description of the optical activity coefficients than the non-SOC approximation.

IV. CONCLUSIONS

We have incorporated spin-orbit coupling into the DFPT methodology for natural optical activity [31] as implemented in ABINIT. Our new approach enables a more realistic and accurate first-principles study of materials such as $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, where SOC-induced contributions can be substantial due to the presence of heavy atoms. We have utilized our new implementation to study the natural optical activity of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ as a function of its ferroelectric distortion from $P\bar{6}$ to $P3$ space groups. We have shown that the magnitude of the optical rotation increases monotonically with ferroelectric distortion, persisting well beyond the double-well minimum into energetically inaccessible regions. Stabilizing such large distortions through chemical or structural [57] engineering is a promising avenue for future work. Beyond renormalizing the ferroelectric double-well as reported in Ref. [14], our work shows that SOC also plays a fundamental role in the optical activity of PGO, where the main SOC-induced effects are electronic in origin, while SOC-driven structural relaxation effects are minor. The two studies together thus provide a consistent picture

of PGO as a material in which the interplay of structural cavities [14], heavy-element chemistry, and chirality gives rise to a remarkably rich set of SOC-driven phenomena, from structural energetics to optical response.

Our results of Sec. III D indicate that, even in nonmagnetic systems like lead germanate, the spin-response to an external magnetic field gives rise to non-negligible contributions to the NOA when SOC is taken into account. Magnetic materials appear to be a particularly favorable scenario in which these contributions become more significant. We anticipate that the methodological advancements presented in this work will be valuable for establishing a full DFPT-based framework for calculating natural optical activity in such systems.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are openly available [58].

APPENDIX: LINEAR-RESPONSE TO A STATIC MAGNETIC FIELD

1. Bare response (no SCF)

We start by considering the following Sternheimer equation [39] to a static ($\omega = 0$) but spatially modulated vector potential, $\mathbf{A}(\mathbf{r}) = \mathbf{A}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}$:

$$(\hat{H}_{\mathbf{k}+\mathbf{q}}^{(0)} + \nu \hat{P}_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{m}\mathbf{k}}^{(0)})|u_{\mathbf{m}\mathbf{k},\mathbf{q}}^{A_\beta}\rangle = -\hat{Q}_{\mathbf{k}+\mathbf{q}}(\hat{H}_{\mathbf{k},\mathbf{q}}^{A_\beta} + i q_a \varepsilon_{\beta ab} \hat{H}^{\mathfrak{B}_b})|u_{\mathbf{m}\mathbf{k}}^{(0)}\rangle, \quad (\text{A1})$$

where ν is a parameter with dimensions of energy that ensures that the left-hand side of the equation does not become singular [59], $\hat{P}_{\mathbf{k}} = \sum_{\mathbf{m}} |u_{\mathbf{m}\mathbf{k}}^{(0)}\rangle \langle u_{\mathbf{m}\mathbf{k}}^{(0)}|$ is the projector onto the occupied states ($\hat{Q}_{\mathbf{k}} = 1 - \hat{P}_{\mathbf{k}}$), $\hat{H}^{\mathfrak{B}_b} = -\frac{1}{2} \hat{\sigma}_b$ is the first-order Hamiltonian associated with a magnetic-field interacting with the spin degrees of freedom, and $\hat{H}_{\mathbf{k},\mathbf{q}}^{A_\beta}$ is the momentum representation of the first-order Hamiltonian (orbital part) to a vector potential [39,43,60]. For our purposes, it is enough to recall that

$$\hat{H}_{\mathbf{k},\mathbf{q}=0}^{A_\beta} = \partial_\beta \hat{H}_{\mathbf{k}}^{(0)}, \quad \left. \frac{\partial \hat{H}_{\mathbf{k},\mathbf{q}}^{A_\beta}}{\partial q_\gamma} \right|_{\mathbf{q}=0} = \frac{1}{2} \partial_{\beta\gamma}^2 \hat{H}_{\mathbf{k}}^{(0)}, \quad (\text{A2})$$

where $\partial_\gamma \equiv \partial/\partial q_\gamma$ and $\partial_{\beta\gamma}^2 \equiv \partial^2/\partial q_\gamma \partial q_\beta$ represent first and second derivatives with respect to the wave vector. For simplicity, SCF contributions are excluded from Eq. (A1) at this stage and will be included later once the magnetic-field perturbation is isolated.

Taking the first derivative of Eq. (A1) with respect to q_γ yields an expression for the wave function response to a gradient of the vector potential, which acquires contributions belonging both to the valence- and conduction-band manifolds (indicated with a bar) [39],

$$|u_{\mathbf{m}\mathbf{k},\gamma}^{A_\beta}\rangle = -\partial_\gamma \hat{P}_{\mathbf{k}} \partial_\beta \hat{P}_{\mathbf{k}} |u_{\mathbf{m}\mathbf{k}}^{(0)}\rangle + |\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{A_\beta}\rangle, \quad (\text{A3})$$

where $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ and $|\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{A_\beta}\rangle$ is a linear-response quantity that fulfills the following Sternheimer equation [39]:

$$(\hat{H}_{\mathbf{k}}^{(0)} + \nu \hat{P}_{\mathbf{k}} - \epsilon_{\mathbf{m}\mathbf{k}}^{(0)})|\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{A_\beta}\rangle = -\hat{Q}_{\mathbf{k}}[\hat{O}_{\mathbf{k}}^{\beta\gamma} + i \varepsilon_{\beta\gamma\delta} \hat{H}^{\mathfrak{B}_\delta}]|u_{\mathbf{m}\mathbf{k}}^{(0)}\rangle, \quad (\text{A4})$$

where

$$|\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{A_\beta}\rangle \equiv \left. \frac{\partial |\bar{u}_{\mathbf{m}\mathbf{k},\mathbf{q}}^{A_\beta}\rangle}{\partial q_\gamma} \right|_{\mathbf{q}=0} \quad (\text{A5})$$

and

$$\hat{O}_{\mathbf{k}}^{\beta\gamma} = \partial_\gamma \hat{H}_{\mathbf{k}}^{(0)} \partial_\beta \hat{P}_{\mathbf{k}} - \partial_\gamma \hat{P}_{\mathbf{k}} \partial_\beta \hat{H}_{\mathbf{k}}^{(0)} + \frac{1}{2} \partial_{\beta\gamma}^2 \hat{H}_{\mathbf{k}}^{(0)}. \quad (\text{A6})$$

The magnetic-field response is captured by the antisymmetric ($\beta \leftrightarrow \gamma$) components of the response. We define the perturbing operator appearing in Eq. (A4) as

$$\hat{T}_{\mathbf{k}}^{\beta\gamma} = \hat{O}_{\mathbf{k}}^{\beta\gamma} + i \varepsilon_{\beta\gamma\delta} \hat{H}^{\mathfrak{B}_\delta}, \quad (\text{A7})$$

where $\hat{T}_{\mathbf{k}}^{\beta\gamma} = \frac{1}{2}(\hat{T}_{\mathbf{k}}^{S,\beta\gamma} + \hat{T}_{\mathbf{k}}^{A,\beta\gamma})$. The symmetric (S) and antisymmetric (A) perturbing operators are given by

$$\begin{aligned} \hat{T}_{\mathbf{k}}^{S,\beta\gamma} &= \partial_\gamma \hat{H}_{\mathbf{k}}^{(0)} \partial_\beta \hat{P}_{\mathbf{k}} - \partial_\gamma \hat{P}_{\mathbf{k}} \partial_\beta \hat{H}_{\mathbf{k}}^{(0)} + \partial_\beta \hat{H}_{\mathbf{k}}^{(0)} \partial_\gamma \hat{P}_{\mathbf{k}} \\ &\quad - \partial_\beta \hat{P}_{\mathbf{k}} \partial_\gamma \hat{H}_{\mathbf{k}}^{(0)} + \partial_{\beta\gamma}^2 \hat{H}_{\mathbf{k}}^{(0)}, \\ \hat{T}_{\mathbf{k}}^{A,\beta\gamma} &= \partial_\gamma \hat{H}_{\mathbf{k}}^{(0)} \partial_\beta \hat{P}_{\mathbf{k}} - \partial_\gamma \hat{P}_{\mathbf{k}} \partial_\beta \hat{H}_{\mathbf{k}}^{(0)} - \partial_\beta \hat{H}_{\mathbf{k}}^{(0)} \partial_\gamma \hat{P}_{\mathbf{k}} \\ &\quad + \partial_\beta \hat{P}_{\mathbf{k}} \partial_\gamma \hat{H}_{\mathbf{k}}^{(0)} + 2i \varepsilon_{\beta\gamma\delta} \hat{H}^{\mathfrak{B}_\delta}. \end{aligned} \quad (\text{A8})$$

We can split the solution of Eq. (A4) into its symmetric and antisymmetric components as

$$|\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{A_\beta}\rangle = \frac{1}{2}(|\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{S,A_\beta}\rangle + |\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{A,A_\beta}\rangle). \quad (\text{A9})$$

It is then easy to check that $|\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{S,A_\beta}\rangle = |\partial_{\beta\gamma}^2 u_{\mathbf{m}\mathbf{k}}^{(0)}\rangle$ and

$$\frac{i}{2} |\bar{u}_{\mathbf{m}\mathbf{k},\gamma}^{A,A_\beta}\rangle = -\varepsilon_{\beta\gamma\delta} (|\bar{u}_{\mathbf{m}\mathbf{k}}^{B_\delta}\rangle + |\bar{u}_{\mathbf{m}\mathbf{k}}^{\mathfrak{B}_\delta}\rangle) = \varepsilon_{\gamma\beta\delta} |\bar{u}_{\mathbf{m}\mathbf{k}}^{\mathfrak{B}_\delta}\rangle, \quad (\text{A10})$$

where we have defined the perturbing operator for the orbital part of a magnetic-field as

$$\hat{O}_{\mathbf{k}}^{B_c} = -\frac{i}{2} \varepsilon_{abc} \{\partial_a \hat{P}_{\mathbf{k}}, \partial_b \hat{H}_{\mathbf{k}}^{(0)}\}, \quad (\text{A11})$$

where $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. The total magnetic-field response contains contributions from the valence-band manifold coming from the first term on the right-hand side of Eq. (A3), which play an important role once SCF contributions are included (see the next subsection). Note that the definition for the operator $\hat{O}_{\mathbf{k}}^{B_c}$ given by Eq. (A11) differs by a minus

sign from the convention adopted in Ref. [31]. This is why the order of the indices in the Levi-Civita symbol is changed in the $\mathcal{A}$ terms between Ref. [31] and the present work. In addition, we have identified a typographical error in Eq. (17) of Ref. [31], where the half factor should not appear; this has been corrected in our Eqs. (15b) and (22).

2. Self-consistent response

Self-consistency in the magnetic-field response is enforced by incorporating the first-order potential $\hat{V}^{B_c}$ into its corresponding Sternheimer equation. Writing down the operators explicitly,

$$\begin{aligned} & (\hat{H}_{\mathbf{k}}^{(0)} + v\hat{P}_{\mathbf{k}} - \epsilon_{m\mathbf{k}}^{(0)})|\tilde{u}_{m\mathbf{k}}^{B_c}\rangle \\ &= -\hat{Q}_{\mathbf{k}}\left(-\frac{i}{2}\varepsilon_{abc}\{\partial_a\hat{P}_{\mathbf{k}}, \partial_b\hat{H}_{\mathbf{k}}^{(0)}\} - \frac{1}{2}\hat{\sigma}_c + \hat{V}^{B_c}\right)|u_{m\mathbf{k}}^{(0)}\rangle, \end{aligned} \quad (\text{A12})$$

where

$$V^{B_c}(\mathbf{r}) = \int K_{\text{Hxc}}(\mathbf{r}, \mathbf{r}') n^{B_c}(\mathbf{r}) d^3r'. \quad (\text{A13})$$

In the last equation, $K_{\text{Hxc}}(\mathbf{r}, \mathbf{r}')$ is the Hartree and exchange-correlation (Hxc) kernel, which is a 4×4 matrix. The first-order electron density appearing in Eq. (A13) can be written as the following trace in spinor space [44,61]:

$$n^{B_c}(\mathbf{r}) = \frac{1}{2} \text{Tr} \left[\sigma \int_{\text{BZ}} [d^3k] \sum_m f_{m\mathbf{k}} (\langle \mathbf{r} | u_{m\mathbf{k}}^{B_c} \rangle \langle u_{m\mathbf{k}}^{(0)} | \mathbf{r} \rangle + \text{H.c.}) \right]. \quad (\text{A14})$$

Here, “H.c.” denotes Hermitian conjugation, and $\sigma = (\sigma_0, \sigma_x, \sigma_y, \sigma_z)$ collects the 2×2 identity matrix σ_0 together with the Pauli matrices σ_i ($i = x, y, z$). Similarly, $n^{B_c} = (n_0^{B_c}, n_x^{B_c}, n_y^{B_c}, n_z^{B_c})$ is a 4-vector. To emphasize the role of the valence-band contributions in the magnetic-field response discussed above, let us explicitly write the first-order wavefunction response as

$$|u_{m\mathbf{k}}^{B_c}\rangle = -i\varepsilon_{abc}\partial_a\hat{P}_{\mathbf{k}}\partial_b\hat{P}_{\mathbf{k}}|u_{m\mathbf{k}}^{(0)}\rangle + |\tilde{u}_{m\mathbf{k}}^{B_c}\rangle. \quad (\text{A15})$$

Substituting this expression into Eq. (A14) yields

$$\begin{aligned} n^{B_c}(\mathbf{r}) = & \frac{1}{2} \text{Tr} \left[\sigma \int_{\text{BZ}} [d^3k] \sum_m f_{m\mathbf{k}} (\langle \mathbf{r} | \tilde{u}_{m\mathbf{k}}^{B_c} \rangle \langle u_{m\mathbf{k}}^{(0)} | \mathbf{r} \rangle + \text{H.c.}) \right] \\ & - \frac{i}{2} \varepsilon_{abc} \text{Tr} \left[\sigma \int_{\text{BZ}} [d^3k] \sum_{m,n} f_{m\mathbf{k}} (\langle \mathbf{r} | u_{n\mathbf{k}}^{(0)} \rangle \langle \partial_a u_{n\mathbf{k}}^{(0)} | \partial_b u_{m\mathbf{k}}^{(0)} \rangle \langle u_{m\mathbf{k}}^{(0)} | \mathbf{r} \rangle + \text{H.c.}) \right]. \end{aligned} \quad (\text{A16})$$

The first term is the usual DFPT density-response contribution, given by ground-state Bloch functions and their first-order (Sternheimer-like) corrections. The second term arises in the particular case of a magnetic-field perturbation, specifically its orbital part, and involves covariant $\mathbf{k}$ -derivatives of Bloch states, yielding an orbital Berry-curvature-type contribution to the density response. Note that, in time-reversal symmetric insulators, the latter

contribution is nonzero only in the spin components of the density response, $(n_x^{B_c}, n_y^{B_c}, n_z^{B_c})$, while the charge component $n_0^{B_c}$ vanishes identically. In practice, and according to the implementation limitations discussed in Sec. III A, these additional contributions to the density-response and the induced first-order SCF potential—see Eq. (A13)—are currently accessible in ABINIT (v10.6.5) only within the LDA XC approximation.

- [1] H. Iwasaki, K. Sugii, T. Yamada, and N. Niizeki, 5PbO · 3GeO₂ crystal; A new ferroelectric, *Appl. Phys. Lett.* **18**, 444 (1971).
- [2] S. Nanamatsu, H. Sugiyama, K. Doi, and Y. Kondo, Ferroelectricity in Pb₅Ge₃O₁₁, *J. Phys. Soc. Jpn.* **31**, 616 (1971).
- [3] E. Bousquet, M. Fava, Z. Romestan, F. Gómez-Ortiz, E. E. McCabe, and A. H. Romero, Structural chirality and related properties in the periodic inorganic solids: Review and perspectives, *J. Phys.: Condens. Matter* **37**, 163004 (2025).
- [4] S. Ivanov, A. Stash, and T. Sorokin, New investigations of the crystal structure of lead germanate Pb₅Ge₃O₁₁, *Crystallogr. Rep.* **67**, 334 (2022).
- [5] M. I. Kay, R. E. Newnham, and R. W. Wolfe, The crystal structure of the ferroelectric phase of Pb₅Ge₃O₁₁, *Ferroelectrics* **9**, 1 (1975).
- [6] M. Fava, W. Lafargue-Dit-Hauret, A. H. Romero, and E. Bousquet, Ferroelectricity and chirality in the Pb₅Ge₃O₁₁ crystal, *Phys. Rev. B* **109**, 024113 (2024).

- [7] M. Conroy, D. R. Småbråten, C. Ophus, K. Shapovalov, Q. M. Ramasse, K. A. Hunnestad, S. M. Selbach, U. Aschauer, K. Moore, J. M. Gregg, U. Bangert, M. Stengel, A. Gruverman, and D. Meier, Observation of antiferroelectric domain walls in a uniaxial hyperferroelectric, *Adv. Mater.* **36**, 2405150 (2024).
- [8] O. Bak, T. S. Holstad, Y. Tan, H. Lu, D. M. Evans, K. A. Hunnestad, B. Wang, J. P. V. McConville, P. Becker, L. Bohatý, I. Lukyanchuk, V. M. Vinokur, A. T. J. van Helvoort, J. M. Gregg, L.-Q. Chen, D. Meier, and A. Gruverman, Observation of unconventional dynamics of domain walls in uniaxial ferroelectric lead germanate, *Adv. Funct. Mater.* **30**, 2000284 (2020).
- [9] Y. Tikhonov, J. R. Maguire, C. J. McCluskey, J. P. V. McConville, A. Kumar, H. Lu, D. Meier, A. Razumnaya, J. M. Gregg, A. Gruverman, V. M. Vinokur, and I. Luk'yanchuk, Polarization topology at the nominally charged domain walls in uniaxial ferroelectrics, *Adv. Mater.* **34**, 2203028 (2022).

- [10] T. Yamada, H. Iwasaki, and N. Niizeki, Elastic and piezoelectric properties of ferroelectric $5\text{PbO} \cdot 3\text{GeO}_2$ crystals, *J. Appl. Phys.* **43**, 771 (1972).
- [11] T. Li, S. T. Hsu, B. Ulrich, H. Ying, L. Stecker, D. Evans, Y. Ono, J.-s. Maa, and J. J. Lee, Fabrication and characterization of a $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ one-transistor-memory device, *Appl. Phys. Lett.* **79**, 1661 (2001).
- [12] O. G. Vlokh, L. A. Lazgko, and Y. I. Shopa, Electrooptic and electrogyration properties of the solid solutions on the basis of lead germanate, *Phys. Status Solidi A* **65**, 371 (1981).
- [13] D. Adamenko, I. Klymiv, V. M. Duda, R. Vlokh, and O. Vlokh, Electrogyration and Faraday rotation in pure and Cr-doped lead germanate crystals, *J. Phys.: Condens. Matter* **20**, 075201 (2008).
- [14] M. Fava, W. Lafargue-Dit-Hauret, A. H. Romero, and E. Bousquet, Large and tunable spin-orbit effect of $6p$ orbitals through structural cavities in crystals, *Phys. Rev. B* **108**, L201112 (2023).
- [15] K. Aizu, Reversal in optical rotatory power—"Gyroelectric" crystals and "hypergyroelectric" crystals, *Phys. Rev.* **133**, A1584 (1964).
- [16] V. A. Kizel', Y. I. Krasilov, and V. I. Burkov, Experimental studies of gyrotropy of crystals, *Sov. Phys. Usp.* **17**, 745 (1975).
- [17] C. Konak, V. Kopsky, and F. Smutny, Gyrotropic phase transitions, *J. Phys. C* **11**, 2493 (1978).
- [18] V. K. Wadhawan, Gyrotropy: An implicit form of ferroicity, *Acta Crystallogr. A* **35**, 629 (1979).
- [19] V. K. Wadhawan, Ferroelasticity and related properties of crystals, *Phase Trans.* **3**, 3 (1982).
- [20] T. Hayashida, K. Matsumoto, and T. Kimura, Large electrogyration effect in ferroaxial NiTiO_3 at near infrared wavelengths, *Adv. Opt. Mater.* **13**, 2500364 (2025).
- [21] L. Landau and E. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, New York, 1984), Vol. 8.
- [22] Č. Koňák, J. Fousek, and H. Kürsten, Induced and spontaneous optical activity in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ single crystals, *Ferroelectrics* **21**, 347 (1978).
- [23] H. Iwasaki, K. Sugii, N. Niizeki, and H. T. and, Switching of optical rotatory power in ferroelectric $5\text{PbO} \cdot 3\text{GeO}_2$ single crystal, *Ferroelectrics* **3**, 157 (1972).
- [24] H. Zhong, Z. H. Levine, D. C. Allan, and J. W. Wilkins, Optical activity of selenium: A nearly first-principles calculation, *Phys. Rev. Lett.* **69**, 379 (1992).
- [25] H. Zhong, Z. H. Levine, D. C. Allan, and J. W. Wilkins, Band-theoretic calculations of the optical-activity tensor of α -quartz and trigonal Se, *Phys. Rev. B* **48**, 1384 (1993).
- [26] A. Malashevich and I. Souza, Band theory of spatial dispersion in magnetoelectrics, *Phys. Rev. B* **82**, 245118 (2010).
- [27] Ó. Pozo Ocaña and I. Souza, Multipole theory of optical spatial dispersion in crystals, *SciPost Phys.* **14**, 118 (2023).
- [28] X. Wang and Y. Yan, Optical activity of solids from first principles, *Phys. Rev. B* **107**, 045201 (2023).
- [29] A. Urru, I. Souza, O. P. Ocaña, S. S. Tsirkin, and D. Vanderbilt, Optical spatial dispersion via Wannier interpolation, *Phys. Rev. B* **112**, 045201 (2025).
- [30] X. Wang and Y. Yan, *Ab initio* theory of optical activity in α -quartz in the *GW*-Bethe-Salpeter-equation framework, *Phys. Rev. Lett.* **136**, 186901 (2026).
- [31] A. Zabalo and M. Stengel, Natural optical activity from density-functional perturbation theory, *Phys. Rev. Lett.* **131**, 086902 (2023).
- [32] M. J. Verstraete, J. Abreu, G. E. Allemand, B. Amadon, G. Antonius, M. Azizi, L. Baguet, C. Barat, L. Bastogne, R. Béjaud, J.-M. Beuken, J. Bieder, *et al.*, Abinit 2025: New capabilities for the predictive modeling of solids and nanomaterials, *J. Chem. Phys.* **163**, 164126 (2025).
- [33] X. Gonze, B. Amadon, G. Antonius, F. Arnardi, L. Baguet, J.-M. Beuken, J. Bieder, F. Bottin, J. Bouchet, E. Bousquet, *et al.*, The Abinit project: Impact, environment and recent developments, *Comput. Phys. Commun.* **248**, 107042 (2020).
- [34] V. M. Agranovich and V. Ginzburg, *Crystal Optics with Spatial Dispersion, and Excitons* (Springer-Verlag, New York, 1984).
- [35] J. Jerphagnon and D. S. Chemla, Optical activity of crystals, *J. Chem. Phys.* **65**, 1522 (1976).
- [36] E. Ivchenko, S. Permogorov, and A. Sel'kin, Optical activity of CdS crystals in exciton spectral region, *Solid State Commun.* **28**, 345 (1978).
- [37] Moreover, unless light propagates parallel to the optic axis, optical rotation acquires contributions from both the NOA and the birefringence [34]. Because birefringence is typically orders of magnitude stronger than NOA, isolating the latter is challenging. Therefore, optical activity measurements in PGO are generally performed with light propagating along the optic axis, where birefringence vanishes, allowing for a direct measurement of the g_{33} tensor component [53,55].
- [38] X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Côté, *et al.*, ABINIT: First-principles approach to material and nanosystem properties, *Comput. Phys. Commun.* **180**, 2582 (2009).
- [39] M. Royo and M. Stengel, First-principles theory of spatial dispersion: Dynamical quadrupoles and flexoelectricity, *Phys. Rev. X* **9**, 021050 (2019).
- [40] Note that $\hat{H}_k^{k\gamma} = \hat{H}_k^{k\gamma}$ and we can set $\hat{H}_k^{\varepsilon\alpha} = \hat{V}^{\varepsilon\alpha}$ in all of our equations, since $\hat{H}_k^{\varepsilon\alpha}$ is a purely "cross-gap" operator.
- [41] Y. Yafet, *g Factors and Spin-lattice Relaxation of Conduction Electrons* (Academic, New York, 1963), pp. 1–98.
- [42] S. Zhong, J. E. Moore, and I. Souza, Gyrotropic magnetic effect and the magnetic moment on the Fermi surface, *Phys. Rev. Lett.* **116**, 077201 (2016).
- [43] A. M. Essin, A. M. Turner, J. E. Moore, and D. Vanderbilt, Orbital magnetoelectric coupling in band insulators, *Phys. Rev. B* **81**, 205104 (2010).
- [44] F. Ricci, S. Prokhorenko, M. Torrent, M. J. Verstraete, and E. Bousquet, Density functional perturbation theory within non-collinear magnetism, *Phys. Rev. B* **99**, 184404 (2019).
- [45] Prior to the study of PGO, we validated the new expression for the NOA, using Eq. (26), in the absence of SOC for α - SiO_2 , α - HgS , and trigonal Se. In all cases, the calculated gyration coefficients agreed with those obtained using the existing implementation to machine precision.
- [46] Note, however, that the magnetic field perturbation now acts on both the orbital and spin degrees of freedom.
- [47] M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonze, and G.-M. Rignanese, The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table, *Comput. Phys. Commun.* **226**, 39 (2018).

- [48] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [49] Y. Iwata, Neutron diffraction study of the structure of paraelectric phase of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, *J. Phys. Soc. Jpn.* **43**, 961 (1977).
- [50] Y. V. Shaldin, A. A. Bush, S. Matyjasik, and M. K. Rabadanov, Characteristic of spontaneous polarization in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystals, *Crystallogr. Rep.* **50**, 836 (2005).
- [51] K. Sugii, H. Iwasaki, and S. Miyazawa, Crystal growth and some properties of $5\text{PbO} \cdot 3\text{GeO}_2$ single crystals, *Mater. Res. Bull.* **6**, 503 (1971).
- [52] J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B* **45**, 13244 (1992).
- [53] H. Iwasaki, S. Miyazawa, H. Koizumi, K. Sugii, and N. Niizeki, Ferroelectric and optical properties of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and its iso-morphous compound $\text{Pb}_5\text{Ge}_2\text{SiO}_{11}$, *J. Appl. Phys.* **43**, 4907 (1972).
- [54] Experimental values at $T = 0\text{ K}$ in Table IV were obtained by graphical extrapolation of the data in Refs. [53,55], and thus should be regarded as approximate references only.
- [55] D. Adamenko and R. Vlokh, Critical exponents of the order parameter of diffuse ferroelectric phase transitions in the solid solutions based on lead germanate: Studies of optical rotation, *Condens. Matter Phys.* **25**, 43703 (2022).
- [56] F. Jäger, N. A. Spaldin, and S. Bhowal, Universal responses in nonmagnetic polar metals, *Phys. Rev. Res.* **6**, 013251 (2024).
- [57] W. Luo, A. Zabalo, G. Ren, G.-Y. Jung, M. Stengel, R. Mishra, J. Ravichandran, and L. Bellaiche, Strain-induced gyrotropic effects in ferroelectric BaTiS_3 , *Phys. Rev. B* **113**, L100101 (2026).
- [58] A. Zabalo, M. Stengel, and E. Bousquet, Data and plotting scripts, https://github.com/azabaloa/PGO_data.git.
- [59] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Phonons and related crystal properties from density-functional perturbation theory, *Rev. Mod. Phys.* **73**, 515 (2001).
- [60] C. E. Dreyer, M. Stengel, and D. Vanderbilt, Current-density implementation for calculating flexoelectric coefficients, *Phys. Rev. B* **98**, 075153 (2018).
- [61] M. Royo and M. Stengel, Dynamical response of noncollinear spin systems at constrained magnetic moments, *Phys. Rev. X* **16**, 011049 (2026).