

Electric polarization driven by noncollinear spin alignment investigated by first principles calculations

Sergiy Mankovsky^{1,2,*}, Svitlana Polesya², Jan Minar³, Hongbin Zhang¹, and Hubert Ebert²

¹*Institute of Materials Science, TU Darmstadt, 64287 Darmstadt, Germany*

²*Department of Chemistry/Phys. Chemistry, LMU Munich, Butenandtstrasse 11, D-81377 Munich, Germany*

³*New Technologies Research Center, University of West Bohemia in Pilsen, 30100 Pilsen, Czech Republic*



(Received 5 December 2025; accepted 18 August 2026; published 21 September 2026)

We present an approach for first principles investigations on the spin-driven electric polarization in type II multiferroics. We propose a parametrization of the polarization with the parameters calculated using the Korringa-Kohn-Rostoker Green's function (KKR-GF) formalism. Within this approach the induced electric polarization of a unit cell is represented in terms of three-site parameters. Those antisymmetric with respect to spin permutation are seen as an *ab initio* based counterpart to the phenomenological parameters used within the inverse-Dzyaloshinskii-Moriya-interaction (DMI) model. Due to their relativistic origin, these parameters are responsible for the electric polarization induced in the presence of a noncollinear spin alignment in materials with a centrosymmetric crystal structure. Beyond this, our approach gives direct access to the element- or site-resolved electric polarization. To demonstrate the capability of the approach, we consider several examples of the so-called type II multiferroics, for which the magnetoelectric effect is observed either as a consequence of an applied magnetic field (we use Cr_2O_3 as a prototype), or as a result of a phase transition to a spin-spiral magnetic state, as for instance in MnI_2 , CuCrO_2 , and AgCrO_2 .

DOI: [10.1103/9fs1-5gxq](https://doi.org/10.1103/9fs1-5gxq)

I. INTRODUCTION

The growing interest in multiferroic materials is motivated by the possibility to control their magnetic or electric polarization by applying external electric or magnetic fields, respectively [1–4]. This allows various technical applications in electronics, spintronics, etc. [5]. In particular, applying a static magnetic or electric field to control the properties of multiferroic materials, one can minimize the energy losses caused by induced electric currents. This feature is a consequence of coexisting ferroelectricity (FE) and ferromagnetism (FM) in multiferroic systems, which obey individually different symmetry requirements, either broken space inversion symmetry $\mathcal{I}$ or broken time reversal symmetry $\mathcal{T}$, respectively, however, with the combined $\mathcal{IT}$ symmetry being conserved.

While there are different types of multiferroics discussed in the literature (see, e.g., [2,3,6–8]), we will focus here on the materials which belong to the so-called type-II multiferroics, in which electric polarization appears only in the magnetically ordered phase due to a strong coupling between magnetism and ferroelectricity. Any perturbation in these materials, breaking time reversal symmetry $\mathcal{T}$, gives rise to an electric polarization being allowed as a result of broken

inversion symmetry $\mathcal{I}$ [2,9–11]. This occurs in collinear antiferromagnetic (AFM) systems, where an electric polarization can be induced by an applied magnetic field, as it is observed, for instance, in β Cr_2O_3 [12–14]. In this case, the linear magnetoelectric (ME) effect is described by the ME tensor $\underline{\alpha}$ giving the induced electric polarization $\vec{P}$ via the relationship $\vec{P} = \underline{\alpha}\vec{H}$. As an example for materials exhibiting the spontaneous ME effect, one can mention the triangular-lattice AFM compounds (TLA) such as MnI_2 , CuFeO_2 , CuCrO_2 , AgCrO_2 , etc. These materials undergo a phase transition at low temperature to a noncollinear magnetic state [15–19], as a consequence of the competition of the frustrated AFM exchange interactions. In this work, however, we do not discuss the mechanisms responsible for the stabilization of the AFM state, focusing instead on the electric polarization for different noncollinear magnetic structures.

Despite common symmetry requirements, the microscopic mechanism for the ME effect in the type II multiferroics may differ for different materials [10,20]. The spin-orbit-driven mechanism suggested by Katsura, Nagaosa, and Balatsky (KNB) was interpreted in terms of the spin current [21] appearing between the two spin moments, $\hat{s}_1$ and $\hat{s}_2$, due to their noncollinear alignment. This theory suggests the rule that the induced electric polarization is characterized by the expression $\vec{P}_{12} \sim \vec{e}_{12} \times (\hat{s}_1 \times \hat{s}_2)$ with $\vec{e}_{12} = \vec{R}_{12}/|\vec{R}_{12}|$ ($\vec{R}_{12}$ is the vector connecting the two sites). This rule indeed explains the trend of the ferroelectric behavior for a large number of multiferroics with a cycloidal-type spiral spin order [22–24]. A similar rule was suggested by Mostovoy [9], that was obtained by applying the phenomenological theory of inhomogeneous ferroelectric magnets to systems with cubic symmetry. However, this rule fails to explain the spin-driven

*Contact author: mankovsky@tmm.tu-darmstadt.de

ferroelectricity for instance in triangular-lattice multiferroic helimagnets [25–27], as a consequence of the special symmetry used in these works, implying a cubic environment for the magnetic dimers (see, e.g., Refs. [7,11,28]). For that reason, other mechanisms were suggested to explain the observed magnetoelectric effect in these materials. For instance, the electric polarization in CuFeO_2 having a helimagnetic structure was attributed to the single-ion effect due to the spin-dependent $p-d$ hybridization [7,26].

To go beyond the phenomenological model treatment of the ME effect, a more general approach based on density functional theory (DFT) calculations has been used [23,29,30]. However, a direct DFT-based treatment of the extended spin structures (e.g., long-period spin spirals) requires supercell calculations, which are in general rather time consuming. A simplification can be achieved by the parametrization scheme given for instance by Xiang *et al.* [29] within the generalized KNB model representing the spin-induced polarization in terms of spin-dimer contributions. This approach could be applied successfully to describe the induced electric polarization of various systems with complex spin textures [31–33]. Another generalized KNB formalism has been reported by Solovyev [30], which is based on a parametrization using the Berry-phase theory for the effective half-filled Hubbard model. It was successfully applied to describe the spin-induced electric polarization in different multiferroic materials [11,30,34,35]. Note that these approaches represent the ‘pure electronic’ contribution to the induced polarization. An alternative mechanism was considered by Sergienko and Dagotto [36] to explain the electric polarization in perovskite RMnO_3 ($R = \text{Gd, Tb, Dy}$) having modulated magnetic structure. It postulates an electric polarization appearing due to the spin-orbit-coupling (SOC)-driven atomic displacements induced by the noncollinear spin alignment. This is the so-called ‘lattice-mediated polarization’ mechanism which is discussed in terms of the Dzyaloshinskii-Moriya interaction and may be responsible for the stabilization of helical magnetic order in the presence of atomic displacements that break the inversion symmetry in the system. Accordingly, it is referred to in the literature as the inverse-DMI mechanism. Xiang *et al.* [37] extended their generalized KNB theory by taking into account the ion-displacement contribution to the spin-order induced electric polarization. Its importance for the multiferroics LiCuVO_4 , TbMnO_3 , and HoMnO_3 (exhibiting spin spirals) was then discussed in relation to the electronic contribution. Also in the case of the collinear AFM Cr_2O_3 the ‘lattice mediated polarization’ represents a dominating contribution to the magnetoelectric polarization, as it was demonstrated by different groups [14,38,39].

We will focus in the following on the ‘pure electronic’ effect, using the approach described in Sec. II, representing the parametrization of the electric polarization in full analogy to the parametrization of the spin-lattice Hamiltonian [40,41]. The corresponding parameters are calculated from first principles via the Green’s function (GF) technique implemented using the Korringa-Kohn-Rostoker (KKR) band structure method. In the following sections we apply this approach to different materials, demonstrating the properties which can be discussed on the basis of such calculations. It is worth noting that this approach can be extended

accounting for the lattice-mediated polarization mechanism. This can be achieved by making use of our previous development of a scheme to calculate the spin-lattice coupling constants [40,41]. This issue is briefly considered in Sec. II and in Sec. V, but is beyond the aims of the present work.

II. THEORETICAL DETAILS

In a recent study [40,41] we discussed the spin-lattice interaction represented by the coupling tensors $\underline{J}_{ij,k}$ which allows to get the force on an atom at $\vec{R}_k$ generated due to the perturbation caused by the rotation of the spin moments $\hat{s}_i$ and $\hat{s}_j$ on sites i and j , respectively. Using the same idea for the magnetically induced electric polarization $\Delta\vec{P}$, we start with the definition

$$\Delta\vec{P} = \frac{1}{\Omega} \int d^3r e\vec{r} \Delta\rho(\vec{r}). \quad (1)$$

In the case of a solid with $N_{u.c.}$ atoms per unit cell which are specified by the basis vectors t_q ($q = 1, N_{u.c.}$) and have an associated volume Ω_q , the integral in Eq. (1) can be written as follows,

$$\begin{aligned} \Delta\vec{P} &= \frac{e}{\Omega} \sum_n \sum_q \int_{\Omega_q} d^3r [\vec{r}_q + \vec{R}_n + \vec{t}_q] \Delta\rho(\vec{r}_q) \\ &= \frac{e}{\Omega} \left[\sum_n \sum_q \int_{\Omega_q} d^3r_q \vec{r}_q \Delta\rho(\vec{r}_q) \right. \\ &\quad + \sum_n \vec{R}_n \sum_q \int_{\Omega_q} d^3r_q \Delta\rho(\vec{r}_q) \\ &\quad \left. + \sum_n \sum_q \vec{t}_q \int_{\Omega_q} d^3r_q \Delta\rho(\vec{r}_q) \right]. \end{aligned} \quad (2)$$

Here $\vec{R}_n$ is a Bravais vector that describes the position of the unit cell, and $\vec{r}_q = \vec{r} - \vec{R}_n - \vec{t}_q$ are atom cell centered coordinates. The second term on the right-hand side of Eq. (2) vanishes due to charge neutrality of the unit cell. The third term describes the change of the electric polarization of the unit cell due to a charge redistribution within the cell [42]. This term is not discussed here, as we focus on the polarization due to a charge distortion under the assumption of charge conservation for each atom. Furthermore, the atomic positions described by the Bravais vectors $\vec{R}_n$ are assumed to be fixed, i.e., any atomic displacements are neglected. This implies that the lattice mediated contributions to the induced electric polarization (see, e.g., [36,38,39]) are not taken into account. Accordingly, a direct comparison between the theoretical results presented below to experimental data is not always meaningful. Due to the restriction made, the expression given above can be simplified to the form

$$\Delta\vec{P} \approx \sum_q \frac{1}{\Omega_{u.c.}} \int_{\Omega_q} d^3r_q \vec{r}_q \Delta\rho(\vec{r}_q) = \sum_q \Delta\vec{P}_q, \quad (3)$$

giving the induced electric polarization of a unit cell after summation over the induced electric polarization of all atoms in the cell. This is seen as an on-site approximation assuming a pronounced localization of the electronic states contributing

to the electric polarization of the atoms. As a consequence, for each site q we will discuss the electric polarization evaluated with respect to the site origin and normalized by the unit cell volume, which is induced by all contributions associated with spin rotations on the surrounding atoms i and j .

Although the modern theory of electric polarization is more adequate for periodic systems [43–45], Eq. (1) seems appropriate to describe the polarization in an atomistic real-space formulation, similar to that used in other works based on the generalized KNB model [29,30,33,46]. The present approach is based on the multiple scattering Green's function formalism to represent the electronic structure, which allows to avoid the use of the Bloch theorem for the wave functions. As a natural consequence, the induced charge density $\Delta\rho(\vec{r}_q)$ in Eq. (3), as well as the corresponding induced polarization, will be formulated below as a real space summation over non-periodic contributions induced around distorted spin dimers (i.e., the tilted spin moments). This implies the real-space formulation given by Eq. (1) may be justified by using the correspondence to finite systems, e.g., clusters or molecules. Obviously, the applicability of this approach is determined first of all by the approximations used to go from the expression given by Eq. (1) to that given by Eq. (3).

In general, Eq. (3) obviously may represent the change of the local polarization on lattice site q as a response to a perturbation induced by a rotation of magnetic moments. Here we restrict ourselves to systems with a centrosymmetric crystal lattice and invariant with respect to time reversal in its reference state. This implies that a finite electric polarization may occur only as a consequence of spin rotations creating a noncollinear magnetic structure.

In terms of the electronic Green's function the electric polarization can be written as follows,

$$\Delta\vec{P} = -\frac{1}{\pi} \text{ImTr} \int dE \frac{1}{\Omega_{\text{u.c.}}} \sum_q \int_{\Omega_q} d^3r_q (e\vec{r}_q) \Delta G(\vec{r}_q, \vec{r}_q, E). \quad (4)$$

In the presence of a perturbation $\Delta V(\vec{r})$, the corresponding change of the Green's function occurring in Eq. (4) is given up to second order by

$$\Delta G(E) = G_0(E) \Delta V G_0(E) + G_0(E) \Delta V G_0(E) \Delta V G_0(E) + \dots, \quad (5)$$

with $G_0(E)$ the Green's function of the system in its unperturbed reference state. For the sake of simplicity, we omit the arguments $\vec{r}$ for the potential and Green's functions, keeping in mind an integration over the region of the applied perturbation. In the case of perturbations due to spin tiltings on two lattice sites i and j only the second term in Eq. (5) gives a nonvanishing contribution to the electric polarization, leading to the expression

$$\begin{aligned} \Delta\vec{P} = & -\frac{1}{\pi} \frac{e}{\Omega_{\text{u.c.}}} \text{Im Tr} \int dE \sum_q \\ & \times \int_{\Omega_q} d^3r_q \int d^3r' \int d^3r'' \vec{r}_q G(\vec{r}_q, \vec{r}', E) \Delta V_i(\vec{r}') \\ & \times G(\vec{r}', \vec{r}'', E) \Delta V_j(\vec{r}'') G(\vec{r}'', \vec{r}_q, E). \end{aligned} \quad (6)$$

With this, one can introduce the parameters $p_{ij,k}^{\alpha\beta,\mu}$ defined as derivatives with respect to the spin direction on sites i ($\vec{R}_i = \vec{R}_{n_i} + \vec{t}_{q_i}$) and j ($\vec{R}_j = \vec{R}_{n_j} + \vec{t}_{q_j}$), Δs_i^α and Δs_j^β , respectively, giving the polarization $\vec{P} = (P^x, P^y, P^z)$ on site k with $\vec{R}_k = \vec{t}_{q_k}$ in the unit cell $\vec{R}_{n_k} = 0$, as follows,

$$\begin{aligned} \Delta P^\mu &= \sum_{i,j,k} \frac{\partial^2 (\Delta P_k^\mu) (\{\hat{s}_n\})}{\partial s_i^\alpha \partial s_j^\beta} \Delta s_i^\alpha \Delta s_j^\beta \\ &= \sum_{i,j,k} p_{ij,k}^{\alpha\beta,\mu} \Delta s_i^\alpha \Delta s_j^\beta, \end{aligned} \quad (7)$$

with μ indicating the Cartesian coordinates x, y , and z . Later on we will distinguish symmetric and antisymmetric terms with respect to a permutation of the Cartesian indices α and β .

Similar to the treatment of the spin-lattice coupling parameters [40,41] the KKR-GF formalism allows to express the parameters $\vec{p}_{ij,k}^{\alpha\beta} = (p_{ij,k}^{\alpha\beta,x}, p_{ij,k}^{\alpha\beta,y}, p_{ij,k}^{\alpha\beta,z})$ in terms of the KKR scattering path operator matrix $\underline{\tau}_{ij}(E)$ as follows,

$$\begin{aligned} \vec{p}_{ij,k}^{\alpha\beta} = & -\frac{1}{2\pi} \frac{1}{\Omega_{\text{u.c.}}} \text{Im Tr} \int dE \\ & \times [\langle Z^k | e\vec{r} | Z^k \rangle \underline{\tau}_{ki}^\alpha \underline{\tau}_{ij}^\beta \underline{\tau}_{jk} \\ & + \langle Z^k | e\vec{r} | Z^k \rangle \underline{\tau}_{kj}^\beta \underline{\tau}_{ji}^\alpha \underline{\tau}_{ik}], \end{aligned} \quad (8)$$

with $\hat{\tau}_{ij}(E)$ standing for the scattering path operator that transfers an electronic wave coming in at site j into a wave going out from site i with all possible intermediate scattering events accounted for.

One has to stress that the parameters $\vec{p}_{ij,k}^{\alpha\beta}$ are defined using the same normalization as the induced electric polarization of the unit cell, i.e., both quantities are normalized w.r.t. the volume of the unit cell [see Eqs. (6) and (8)]. With this definition the electric polarization of the unit cell is obtained directly by a summation over the atomic contributions (note that by definition these have to be distinguished from the atomic dipole moments). Using the relativistic spin-angular representation [47], the elements of the matrix $\underline{T}_i^\alpha$ are given by the expression

$$T_{i,\Lambda\Lambda'}^\alpha = \int_{\Omega_q} d^3r Z_{\Lambda'}^{i*}(\vec{r}, E) [\beta \sigma_\alpha B_{xc}(r)] Z_\Lambda^i(\vec{r}, E), \quad (9)$$

and for the elements of the matrix $\langle Z^k | e\vec{r} | Z^k \rangle$ one has

$$\langle Z^k | e\vec{r} | Z^k \rangle_{\Lambda\Lambda'} = \int_{\Omega_q} d^3r Z_{\Lambda'}^{k*}(\vec{r}, E) (e\vec{r}) Z_\Lambda^k(\vec{r}, E), \quad (10)$$

where the four-component wave functions $Z_\Lambda^i(\vec{r}, E)$ stand for the regular solutions of the single-site Dirac equation with the Hamiltonian set up within the framework of relativistic spin-density functional theory [48–50] with $\Lambda = (\kappa, \mu)$, and κ and μ being the spin-orbit and magnetic quantum numbers, β is one of the standard Dirac matrices [47] and $B_{xc}(r)$ is the spin dependent part of the exchange-correlation potential. Note that the energy dependence of the scattering path operator and of the matrices $\underline{T}_i^\alpha$ is omitted in Eq. (8).

By making a decomposition of the polarization parameters into symmetric $p_{ij,k}^{v,s}$ and antisymmetric $\vec{p}_{ij,k}^{v,a}$ parts, one

gets access to the following parametrization of the electric polarization as suggested by Moriya [51] and used later on in generalized KNB theories [11,29,30], which is induced by a spatial spin modulation,

$$\Delta P_k^v = \sum_{ij} [p_{ij,k}^{v,s} \{(\hat{s}_i \cdot \hat{s}_j) - \hat{s}_i^z \hat{s}_j^z\} + \vec{p}_{ij,k}^{v,a} \cdot (\hat{s}_i \times \hat{s}_j) + \hat{s}_i \cdot \underline{\Pi}_{ii,k}^v \hat{s}_i], \quad (11)$$

with $\vec{p}_{ij,k}^{v,a} = (p_{ij,k}^{xv,a}, p_{ij,k}^{yv,a}, p_{ij,k}^{zv,a})$ and $p_{ij,k}^{v,s} = \frac{1}{2} \epsilon_{\alpha\beta\gamma} p_{ij,k}^{\alpha\beta,\gamma}$, where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol and $\gamma = x, y, z$. This approach allows now a general description of the ME effect, giving in particular access to the properties of various compounds avoiding the restrictions caused by phenomenological Hamiltonians (see also discussions by Solovyev *et al.* [11]). This concerns, in particular, the model used to describe the ME effect depending exclusively on the leading exchange mechanism (i.e., direct exchange, superexchange, etc.), while for some materials the exchange interactions may be determined by several mechanisms competing with each other. For instance, two competing types of Cr-Cr exchange interactions are discussed in the case of the TLA compounds $MeCrO_2$, namely, the FM superexchange and AFM direct exchange [52–54].

Furthermore, it is pointed out, that the parameters $p_{ij,k}^{v,s}$ and $\vec{p}_{ij,k}^{v,a}$ are, in general, three-site parameters. They supply the information concerning the individual electric polarization of different atoms k beyond the special case of $k = i$ and $k = j$ with i and j being the site indices for the magnetic atoms with their spin moment rotated.

In the next sections we will focus on the SOC-driven polarization described by the parameters antisymmetric with respect to spin permutation, $\vec{p}_{ij,k}^{v,a}$. These parameters are closely connected to the DMI-like spin-lattice coupling (SLC) parameters discussed in Refs. [40,41], which are responsible for the forces $\mathcal{F}_k^\mu = -\sum_{\alpha,i,j} \mathcal{D}_{ij,k}^{\alpha,\mu} (\hat{e}_i \times \hat{e}_j)_\alpha$ on an atom k in the lattice, arising due to spin canting on sites i and j . These forces appear as a consequence of the electric polarization induced on the sites k [see Eq. (2)]. Their competition with the elastic interatomic forces may lead (as discussed in Refs. [36,37]), or may not lead to atomic displacements. In the former case, the induced local polarization occurs due to the ion displacements and can be treated as a lattice-mediated contribution to the generalized inverse-DMI mechanism. This mechanism is not taken into account in the present work, and accordingly we discuss only the spin-induced polarization appearing in the case of undistorted atomic positions.

III. COMPUTATIONAL DETAILS

All calculations are performed using the fully relativistic KKR Green's function method [55,56]. The exchange-correlation potential is determined within the framework of the general gradient approximation (GGA) to density functional theory (DFT), using the Perdew-Burke-Ernzerhof (PBE) parametrization [57]. A cutoff $l_{\max} = 3$ was used for the angular momentum expansion of the Green's function. Further details can be found, for example, in Refs. [41] and [58]. Integration over the Brillouin zone (BZ) has been performed using a $28 \times 28 \times 15$ $\vec{k}$ -mesh for MnI_2 , a

$22 \times 22 \times 22$ $\vec{k}$ -mesh for $CuCrO_2$, and a $20 \times 20 \times 20$ $\vec{k}$ -mesh for Cr_2O_3 .

The electronic structure and electric polarization parameters for the MnI_2 and $CuCrO_2$ compounds have been calculated within the full-potential approach, i.e., without restrictions to the shape of the electron potential. This scheme implies a space separation by planes dividing the bonds between neighboring atoms, drawn perpendicular to the interatomic vectors. The planes are positioned to divide the bonds in proportion to the atom-dependent radii evaluated using the cross points of Hartree potentials of neighboring atoms. This modified Wigner-Seitz construction gives a space separation very similar to a Bader construction that, however, is much more elaborate. For technical reason, the calculations for Cr_2O_3 have been performed using the atomic sphere approximation (ASA) with the Wigner-Seitz radii $R_{WS}^C = 2.7$ a.u. and $R_{WS}^O = 2.3$ a.u. for Cr and O atoms, respectively.

IV. RESULTS

In the following we present a few representative examples for calculations on the ME effect to demonstrate the application of our approach to several prototype multiferroic systems, comparing the results with the available experimental and theoretical data. The calculations were performed for the triangular-lattice antiferromagnets MnI_2 and $CuCrO_2$ with the spontaneous ferroelectric effect induced by a helimagnetic spin structure and the Cr_2O_3 collinear antiferromagnet exhibiting the linear magnetoelectric effect induced by an external magnetic field. Focusing on the so-called inverse-DMI polarization mechanism described by the second term in Eq. (11), we achieve reasonable agreement of our results with those reported in the literature, obtained using the generalized KNB theory in spite of our restriction to the electronic contribution to the spin-induced electric polarization [11,29,30].

1. MnI_2 First, we consider the triangular-lattice antiferromagnet MnI_2 . It crystallizes in the CdI_2 type structure with centrosymmetric space group $P\bar{3}m1$ (No. 164). Each Mn atomic layer forms a 2D triangular lattice with AFM interatomic interactions leading to a sequence of magnetic phase transitions upon cooling, first at $T_{N1} = 3.95$ K (to the noncollinear magnetic state with a proper-screw spin modulation), then at 3.8 K (T_{N2}) and 3.45 K (T_{N3}) [59]. The in-plane electric polarization of about $84 \mu C/m^2$ emerges in the proper-screw magnetic ground state below T_{N3} , and is characterized by the propagation vector $\vec{q}_{m3} = (0.181, 0, 0.439)$ [27,60].

The parameters $p_{ij,k}^{v,a}$ for MnI_2 , were calculated using Eq. (8) and working in the full-potential mode, i.e., without restrictions for the shape of the electron potential and charge density [50]. Figure 1 shows the vectors (a) $\vec{p}_j^x = (p_{0j,j}^{xx,a}, p_{0j,j}^{xy,a}, p_{0j,j}^{xz,a})$ and (b) $\vec{p}_j^y = (p_{0j,j}^{yx,a}, p_{0j,j}^{yy,a}, p_{0j,j}^{yz,a})$, respectively, characterizing the electric polarization $\vec{P}_j = \vec{p}_j^x \cdot (\hat{s}_0 \times \hat{s}_j)_x$ and $\vec{P}_j = \vec{p}_j^y \cdot (\hat{s}_0 \times \hat{s}_j)_y$ appearing due to the relative rotation of the nearest-neighbor Mn spins for the atoms Mn_j arranged around the central atom Mn_0 . The spin moments are rotated within the planes shown by red circles and are assumed to be the same for every pair of atoms (Mn_0, Mn_j). The spin rotations that break locally the inversion symmetry induce a site-dependent electric polarization for the Mn atoms,

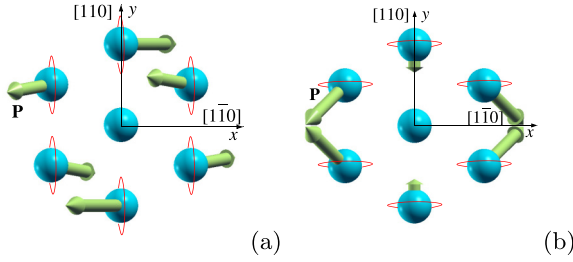


FIG. 1. The polarization vectors (shown by arrows) $\vec{p}_j^x = (p_{0j,j}^{xx,a}, p_{0j,j}^{xy,a}, p_{0j,j}^{xz,a})$ (a) and $\vec{p}_j^y = (p_{0j,j}^{yx,a}, p_{0j,j}^{yy,a}, p_{0j,j}^{yz,a})$ (b) calculated for MnI_2 , characterizing the contributions to the electric polarization due to spin rotation of the nearest-neighbor Mn atoms arranged around Mn_0 . Spin rotations occur within the yz (a) and xz (b) planes shown by red circles.

which depends on the crystal symmetry and the spin rotations, either within the yz and xz planes shown in Figs. 1(a) and 1(b), respectively (a more detailed discussion of the symmetry properties can be found, for instance, in Ref. [11]). In the case of periodic spin modulation, some polarization contributions cancel each other. The total result depends on the type of spin spiral as well as on the direction of propagation vector $\vec{q}$.

Figure 2 shows the polarization for the proper-screw spin modulation with the propagation vectors $\vec{q}_1 \parallel [1\bar{1}0]$ (the x direction) (a) and $\vec{q}_2 \parallel [110]$ (the y directions) (b), plotted as a function of the in-plane propagation vectors $\vec{q}_1 = (q_x, 0, 0)$ and $\vec{q}_2 = (0, q_y, 0)$, respectively. It is nonvanishing in line with the predictions by the generalized KNB models [27,30,60]. The directions of the MnI_2 crystal lattice are characterized by different symmetry: The $[110]$ crystallographic axis is a twofold rotation axis while the plane including the $[1\bar{1}0]$ and the $[001]$ axes (perpendicular to the twofold rotation axis) is a mirror plane. For both propagation vectors $\vec{q}_1$ and $\vec{q}_2$, the nonvanishing electric polarization is aligned along the $\langle 110 \rangle$ crystallographic direction shown schematically in Figs. 2(c) and 2(d), respectively. This is a consequence of symmetry properties of the system in the presence of spatial spin modulation, which is discussed in detail in the literature (see, e.g., Refs. [11,27,30,60]).

As one can see in Fig. 2, the electric polarization of the Mn (blue line) and I (red line) sublattices are comparable in magnitude and changes sign together with the orientation of the propagation vector. Similar trends occur also for the total polarization shown in Fig. 2 by a dashed line; it has a maximum around $q_x = (2\pi/3a)$ (a) and $q_y = (2\pi/3a)$ (b).

Although the propagation vector of the experimentally observed spin spiral has an out-of-plane component $q_z = 0.439(2\pi/c)$, we studied also the electric polarization for the proper-screw spin spiral with different q_z components of the propagation vector. The results are shown in Fig. 2(e) as a function of the in-plane propagation vector $q_{||} = (\xi, 0)(2\pi/a)$, where each curve corresponds to a different value of $q_z = \xi(2\pi/c)$. The red vertical line indicates the wave vector $q_x = \xi(2\pi/3a)$. Figure 2(f) shows the dependence of the electric polarization on the parameter ξ [characterizing the component $q_z = \xi(2\pi/c)$] for the in-plane component $q_x = (1/3)(2\pi/a)$ [indicated by a red line in Fig. 2(e)]. In the case of $q_z = 0.44(2\pi/c)$ the induced electric

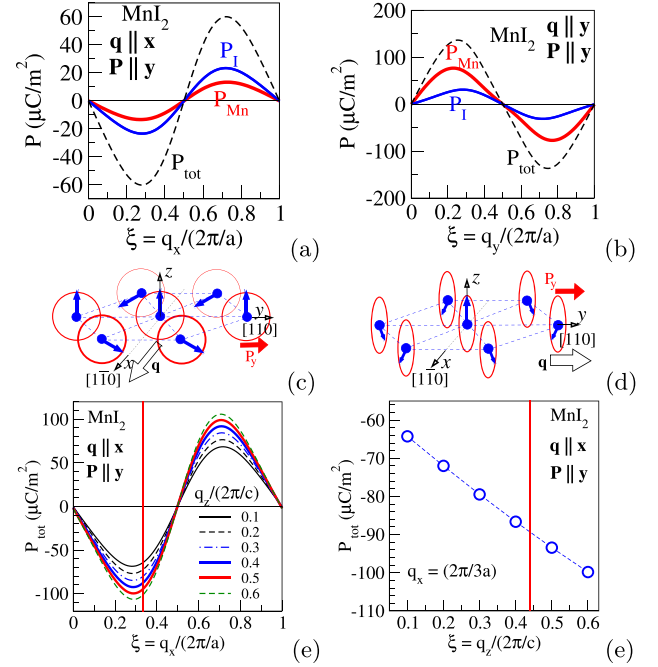


FIG. 2. Element-resolved electric polarization $\vec{P}$ ($\mu\text{C}/\text{m}^2$) in MnI_2 due to proper-screw magnetic structures characterized by propagation vectors $\vec{q} \parallel [1\bar{1}0]$ (a) and $\vec{q} \parallel [110]$ (b), represented as a function of the propagation vector $\vec{q} = (q_x, 0, 0)$ and $\vec{q} = (0, q_y, 0)$, respectively; (c) and (d) show schematically the spin modulation and the directions of the electric polarization $\vec{P}$, corresponding to (a) and (b), respectively; (e) Total electric polarization in MnI_2 due to proper-screw magnetic structures with the out-of-plane propagation vectors $\vec{q} = (q_x, 0, q_z)$, with different curves corresponding to different values of q_z ; (f) The dependence of the electric polarization on q_z for the fixed value of the in-plane component of the propagation vector, $q_x = (2\pi/3a)$.

polarization is equal approximately to $90 \mu\text{C}/\text{m}^2$, which is rather close to the experimental value measured at $T = 2 \text{ K}$ as well as to theoretical results [27] accounting only for the electronic contribution to the polarization. In order to make a one-to-one comparison of their theoretical results (calculated for $T = 0 \text{ K}$) Wu *et al.* [27] extrapolated the experimentally observed polarization to $T = 0 \text{ K}$, leading to an electric polarization of about $128 \mu\text{C}/\text{m}^2$. The deviation from the experimental value was attributed to the contribution due to the lattice mediated polarization, as was confirmed by corresponding calculations.

2. CuCrO_2 As a next example, we discuss the TLA compound CuCrO_2 seen as representative of the MeFeO_2 and MeCrO_2 oxides. For these materials a first-principles treatment of a spin-induced electric polarization (i.e., beyond the phenomenological model consideration) may be challenging because of the competition of two mechanisms of nearest-neighbor exchange interactions, i.e., the FM superexchange and AFM direct exchange. One can expect a corresponding competition also for the magnetoelectric polarization. At room temperature these materials crystallize in the delafossite crystal structure having $R\bar{3}m$ space group symmetry. Their magnetic properties are essentially determined by frustrated antiferromagnetic exchange interactions [17,61]. However,

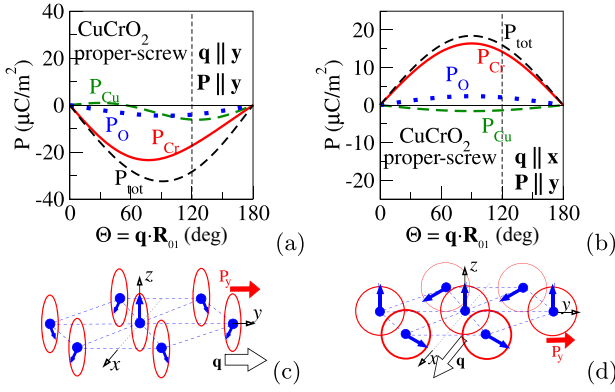


FIG. 3. The $\vec{p}_{ij,k}^{v,a}$ -related electric polarization for the CuCrO_2 compound: on Cu sites (green), Cr sites (red), and O sites (blue). (a) and (b) show the polarization induced by a proper-screw spin modulation characterized by the wave vectors $\vec{q}||\hat{y}||[110]$ and $\vec{q}||\hat{x}||[1\bar{1}0]$, respectively. In both cases a polarization emerges along the y direction. The results are presented as a function of the angle (given in degrees) $\Theta = \vec{q} \cdot \vec{R}_{01}$ where $\vec{R}_{01}$ corresponds to the position of a nearest-neighbor Cr atom at $\vec{R}_{01} = (0.866, 0.5, 0)a$. The proper-screw spin spiral in a 2D triangular Cr sublattice is shown schematically for $\vec{q}||\hat{y}||[110]$ (c) and for $\vec{q}||\hat{x}||[1\bar{1}0]$ (d), respectively. The red arrows show corresponding orientations of the induced electric polarization.

we do not discuss the origin of the magnetic ordering in CuCrO_2 , but only stress that the noncollinear AFM structure at low temperature is accompanied by an emerging electric polarization, similar to the TLA MnI_2 compound.

Previous neutron diffraction studies on CuCrO_2 propose an out-of-plane 120° chiral spin structure below $T_N \sim 24$ K, as the ground state, with a propagation vector $\vec{q} = (1/3, 1/3, 0)$ [62] and incommensurate $\vec{q} = (0.329, 329, 0)$ (either a proper-screw or cycloidal) [63], while an incommensurate proper-screw magnetic structure was suggested in Ref. [64], that corresponds to a slightly modulated 120° spin structure [16]. The observed spontaneous electric polarization appearing below T_N can be attributed to the noncollinear magnetic structure indicating the coupling between the ferroelectricity and spiral magnetic order [25,64–67]. The proper-screw spin modulation with the (110) spiral plane leads to the electric polarization $|\vec{P}| \approx 35 \mu\text{C}/\text{m}^2$ along the $[110]$ direction. An applied magnetic field (above 5.3 T) $\vec{H}||[1\bar{1}0]$ induces a transition to a cycloidal spin structure with a $(1\bar{1}0)$ spiral plane. This leads to a change of the orientation of the electric polarization towards $\vec{P}||[1\bar{1}0]$ [68]. We calculated the electric polarization induced in CuCrO_2 both by the proper-screw as well as by cycloidal spin spirals with the propagation vectors along the (110) and $(1\bar{1}0)$ directions. The results for CuCrO_2 are shown as a function of the angle $\Theta = \vec{q} \cdot \vec{R}_{01}$ (with $\vec{R}_{01}$ the position of a nearest-neighbor Cr atom) in Figs. 3 and 4 for the proper-screw and cycloidal spin modulations, respectively. In the case of a proper-screw spin spiral with the propagation vector $\vec{q}||\hat{y}||[110]$ ($\vec{q}||\hat{y}$), the electric polarization $\vec{P}||[110]$ is nonzero with $\vec{P} \approx 30 \mu\text{C}/\text{m}^2$ for $\Theta = 120^\circ$, in contrast to the prediction by the phenomenological KNB model [21]. In the case of a cycloidal spin spiral the nonvanishing in-plane polarization $\vec{P} \approx 30 \mu\text{C}/\text{m}^2$ is found

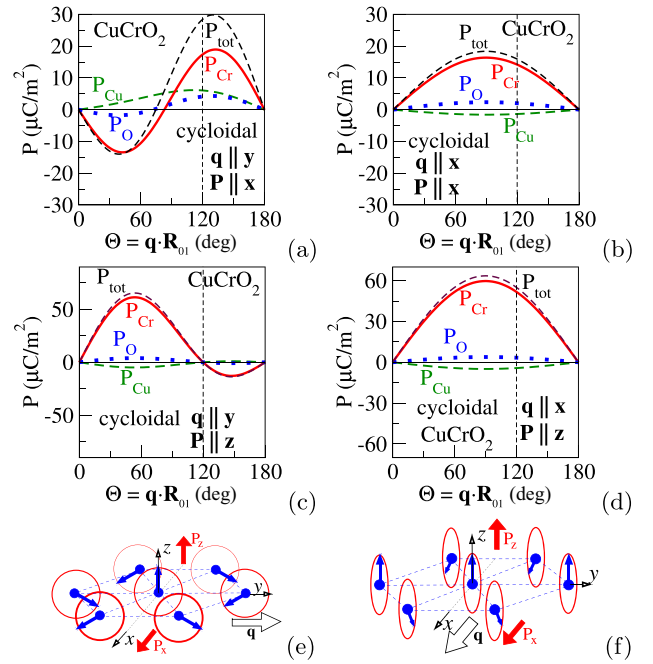


FIG. 4. The $\vec{p}_{ij,k}^{v,a}$ -related electric polarization for the CuCrO_2 compound: on Cu sites (green), Cr sites (red), and O sites (blue). (a) and (c) show the x and z components of the polarization induced by a cycloidal spin modulation characterized by the wave vector $\vec{q}||\hat{y}||[110]$ ($\vec{q}||\hat{y}$). (b) and (d) show the x and z polarization components for a cycloidal spin modulation with $\vec{q}||\hat{x}||[1\bar{1}0]$ ($\vec{q}||\hat{x}$), respectively. The results are presented as a function of the angle (given in degrees) $\Theta = \vec{q} \cdot \vec{R}_{01}$ (similar to Fig. 3). The cycloidal spin modulation in a 2D triangular Cr sublattice is shown schematically for $\vec{q}||\hat{y}||[110]$ (e) and for $\vec{q}||\hat{x}||[1\bar{1}0]$ (f), respectively. The red arrows show corresponding orientations of the induced electric polarization.

parallel to $[1\bar{1}0]$, in line with experiment. These results indicate a dominating contribution due to the inverse-DMI (spin current) mechanism. The remaining difference between the theoretical results and experiment may be ascribed to a possible contribution due to other polarization mechanisms [7]. For the proper-screw spin spiral with $\vec{q}||[1\bar{1}0]$ ($\vec{q}||\hat{x}$) induced electric polarization is orthogonal to $\vec{q}$, i.e., $\vec{P}||[110]$, similar to the results obtained for MnI_2 . In all cases, the electric polarization vanishes at $\Theta = 180^\circ$, when the magnetic moments are getting collinear, changing sign due to a change of the spin spiral chirality. As one can see in Figs. 4(e) and 4(f), cycloidal spin modulation induces also electric polarization along the z direction. Occasionally, the polarization along the z direction almost vanishing at $\Theta = 120^\circ$ in the case of a cycloidal spin modulation with the propagation vector $\vec{q}||[110]$ ($\vec{q}||\hat{y}$) (see more details in Supplemental Material [69]).

The same trend can also be seen for AgCrO_2 [69].

3. Cr_2O_3 Finally, we consider the magnetoelectric properties of Cr_2O_3 , a prototypical material exhibiting the linear ME effect [12,70–72]. Cr_2O_3 crystallizes in the corundum structure with the space group $R\bar{3}c$ (No. 167) [73]. Below $T_N = 310$ K it has an AFM structure with an alternating ‘up-down-up-down’ (*‘udud’*) alignment of the Cr spin moments parallel to the hexagonal c axis of the crystal (or alternatively,

the rhomboidal $\langle 111 \rangle$ direction) [12]. Induced electric ($\vec{P}$) or magnetic ($\vec{M}$) polarization in the crystal appears as a linear response to an applied magnetic $\vec{H}_{\text{ext}}$ or electric $\vec{E}_{\text{ext}}$ field, respectively. The induced polarization is described by the magnetoelectric tensor $\underline{\alpha}$ defined as $\alpha_{\mu\nu}^H = (\partial P_\mu / \partial H_{\text{ext},\nu})$ in the former and $\alpha_{\mu\nu}^E = \mu_0 (\partial M_\mu / \partial E_{\text{ext},\nu})$ in the latter case, with only diagonal elements being nonzero, $\alpha_{xx} = \alpha_{yy} = \alpha_\perp$ and $\alpha_{zz} = \alpha_\parallel$ (see, e.g., [14,71,74]). On a microscopic level, the ME tensor can be obtained on the basis of the DFT, calculating the response either to magnetic or to electric external fields, respectively.

Here we discuss the ME effect of Cr_2O_3 in terms of the parametrization scheme given in Sec. II. We focus on the contributions described by the parameters $p_{ij,k}^{\gamma\nu,a}$, which are antisymmetric w.r.t. spin permutation. The parameters are calculated making use of Eq. (8), and then applied to the calculation of the electric polarization induced by an external magnetic field via Eq. (7). The latter step implies spin rotations for the Cr atoms on sites i by an angle Θ_i according to $(\sin(\Theta_i), 0, \cos(\Theta_i))$, seen as a consequence of an applied magnetic field $\vec{H}_{\text{ext}} = (H_x, 0, 0)$. The electric polarization of the unit cell is obtained as a response to such spin rotations, by summing over all induced electric polarizations corresponding to ‘magnetic’ (Cr) as well as to ‘nonmagnetic’ (O) atoms, according to the expression in Eq. (7). When the magnetic field is assumed to be applied along the x direction, the nonzero contribution to the polarization stems from the parameters $p_{ij,k}^{\gamma\nu,a}$ (i.e., the component parallel to $\hat{s}_i \times \hat{s}_j$) with the index ν indicating the components of the polarization vector.

The components P^x , P^y , and P^z of the induced electric polarization of the sublattices associated to different Cr atoms are plotted as a function of the tilting angle Θ in Fig. 8 in the Supplemental Material [69]. The equilibrium angle Θ corresponding to an imposed external magnetic field H_{ext} was found using the Heisenberg model with the calculated Cr spin moment $M = 2.5\mu_B$ and the Cr-Cr exchange coupling parameters [69]. Using these results, Figs. 5(b) and 5(d), represent the element projected polarization components P^x , P^y , and P^z as a function of the external magnetic field H_{ext} . Panels (a) and (c) show schematically the orientation of the polarization vectors in the unit cell. Note that we consider here two types of an AFM spin alignment in the unit cell, following the discussions in Ref. [30]. Figures 5(a) and 5(b), show the results for the system with the ground state spin configuration ‘*udud*’, which is invariant w.r.t. the combined $\mathcal{IT}$ symmetry operation. One can see an identical polarization of the Cr1 and Cr3 atoms which differ from the polarization of the Cr2 and Cr4 atoms due to the opposite sign of their P^y components. However, the sum over all Cr atoms in the unit cell is finite and negative, while the P^z component is equal to 0 for all atoms. Furthermore, the solid brown line in Fig. 5(b) represents the total polarization in the unit cell accounting for the contributions from the O atoms, indicating its strong enhancement due to the electric polarization of the O atoms.

The down-up-up-down (‘*duud*’) spin alignment [see Figs. 5(c) and 5(d)] corresponds to the system invariant w.r.t. the inversion operation $\mathcal{I}$, for which the electric polarization should be forbidden by symmetry. This is seen in Fig. 5(c), showing that the electric polarization induced on different Cr

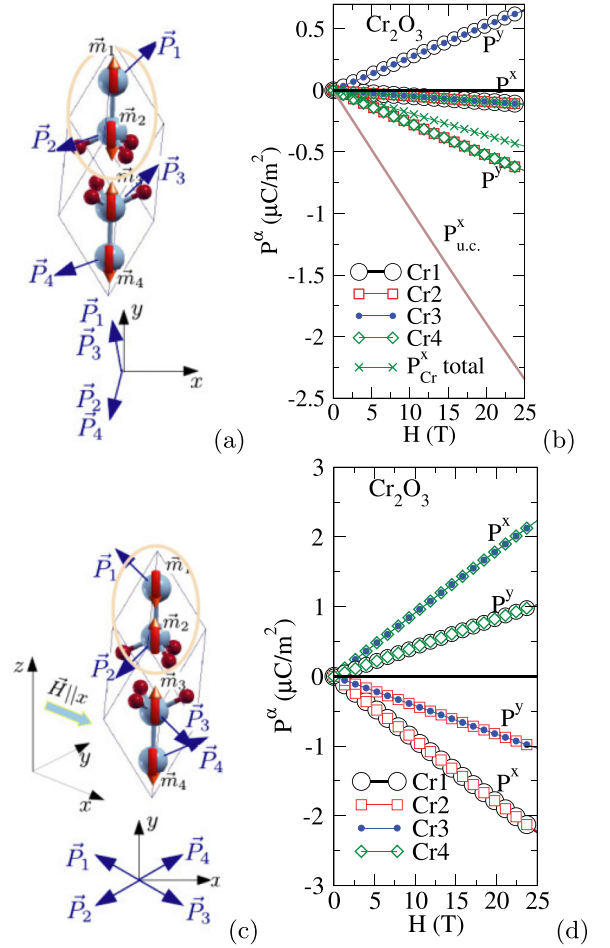


FIG. 5. Element-resolved induced electric polarization in Cr_2O_3 for the spin configurations ‘*udud*’ (upper panel) and ‘*duud*’ (lower panel) (see text). (b) and (d) show the P^x and P^y components of the induced electric polarization of Cr atoms represented as a function of the tilting angle Θ . (a) and (c) show schematically the orientation of the polarization vectors in the unit cell (blue arrows).

atoms are finite but cancel each other when summing up over the unit cell, in line with the discussions by Solovyev [30]. This is expected from symmetry considerations, as this spin configuration ensures that the field-induced spin rotations do not break inversion symmetry in the system.

Coming back to the ground state ‘*udud*’ spin configuration, one can estimate the element $\alpha_\perp^H = (\partial P_x / \partial H_{\text{ext},x})$ of the ME tensor using the total polarization per unit cell shown in Fig. 5(b). This leads to the value $\alpha_\perp^H \approx -0.12 \text{ ps/m}$, which strongly underestimates the experimental value that is in line with other DFT-based calculations demonstrating leading contribution of the lattice mediated contribution to the total electric polarization [14,13]. Note that the estimation based on the polarization of the Cr sublattices only gives $\alpha_\perp \approx -0.024 \text{ ps/m}$, which is substantially smaller and underestimates the available experimental data.

V. SUMMARY AND OUTLOOK

In summary, we present in this work an approach to describe the ME effect in insulating antiferromagnets on a

first-principles level. This is of relevance first of all for materials with an extended noncollinear magnetic structure, for which the developed real-space parametrization scheme will in general be rather efficient, as it allows to avoid time-consuming supercell calculations. The approach presented may be seen as a generalization of the spin-current KNB model, giving a more complete description of the electronic contribution to the induced electric polarization in real materials. The results calculated for several representative materials are in full agreement with other theoretical results obtained using different generalization schemes for the KNB model.

A great benefit of using the KKR Green's function formalism as a basis for our approach is that it allows a number of extensions in various directions. One is the treatment of disordered systems using the coherent potential Approximation (CPA) alloy theory. This can be exploited to study not only disordered alloys, but also the temperature dependence of the ME parameters by using the alloy analogy model (AAM) [75]. Another important issue is the impact of atomic displacements. This aspect was accounted for recently for the exchange coupling constants leading to a scheme to calcu-

late the spin-lattice coupling constants [40,41]. On that basis, another extension can be done for the approach presented here allowing a description of the lattice-mediated polarization mechanism for the ME omitted so far. Work along these directions is in progress.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the computing time provided to them on the high-performance computer Lichtenberg at the NHR Centers NHR4CES at TU Darmstadt. J.M. was supported by the project Quantum materials for applications in sustainable technologies (QM4ST), funded as Project No. CZ.02.01.01/00/22_008/0004572 by P JAK, called Excellent Research.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

-
- [1] G. A. Smolenskii and I. E. Chupis, Ferroelectromagnets, *Phys. Usp.* **25**, 475 (1982).
 - [2] D. Khomskii, Classifying multiferroics: Mechanisms and effects, *Physics Online J.* **2**, 20 (2009).
 - [3] A. P. Pyatakov and A. K. Zvezdin, Magnetoelectric and multiferroic media, *Phys. Usp.* **55**, 557 (2012).
 - [4] N. Ortega, A. Kumar, J. F. Scott, and R. S. Katiyar, Multifunctional magnetoelectric materials for device applications, *J. Phys.: Condens. Matter* **27**, 504002 (2015).
 - [5] X. Liang, H. Chen, and N. X. Sun, Magnetoelectric materials and devices, *APL Mater.* **9**, 041114 (2021).
 - [6] S.-W. Cheong and M. Mostovoy, Multiferroics: A magnetic twist for ferroelectricity, *Nat. Mater.* **6**, 13 (2007).
 - [7] Y. Tokura, S. Seki, and N. Nagaosa, Multiferroics of spin origin, *Rep. Prog. Phys.* **77**, 076501 (2014).
 - [8] E. Bousquet and A. Cano, Non-collinear magnetism and multiferroicity: The perovskite case, *Phys. Sci. Rev.* **8**, 479 (2023).
 - [9] M. Mostovoy, Ferroelectricity in spiral magnets, *Phys. Rev. Lett.* **96**, 067601 (2006).
 - [10] M. Mostovoy, K. Nomura, and N. Nagaosa, Theory of electric polarization in multiorbital Mott insulators, *Phys. Rev. Lett.* **106**, 047204 (2011).
 - [11] I. V. Solovyev, Basic aspects of ferroelectricity induced by noncollinear alignment of spins, *Condens. Matter* **10**, 21 (2025).
 - [12] D. Astrov, Magnetoelectric effect in chromium oxide, *Sov. Phys.-JETP* **13**, 729 (1961).
 - [13] A. Malashevich, S. Coh, I. Souza, and D. Vanderbilt, Full magnetoelectric response of Cr_2O_3 from first principles, *Phys. Rev. B* **86**, 094430 (2012).
 - [14] E. Bousquet, E. Lelievre-Berna, N. Qureshi, J.-R. Soh, N. A. Spaldin, A. Urru, X. H. Verbeek, and S. F. Weber, On the sign of the linear magnetoelectric coefficient in Cr_2O_3 , *J. Phys.: Condens. Matter* **36**, 155701 (2024).
 - [15] H. Yamaguchi, S. Ohtomo, S. Kimura, M. Hagiwara, K. Kimura, T. Kimura, T. Okuda, and K. Kindo, Spiral-plane flop probed by ESR in the multiferroic triangular-lattice antiferromagnet CuCrO_2 , *Phys. Rev. B* **81**, 033104 (2010).
 - [16] M. Frontzek, G. Ehlers, A. Podlesnyak, H. Cao, M. Matsuda, O. Zaharko, N. Aliouane, S. Barilo, and S. V. Shiryayev, Magnetic structure of CuCrO_2 : A single crystal neutron diffraction study, *J. Phys.: Condens. Matter* **24**, 016004 (2012).
 - [17] K. Park, J. Oh, J. C. Leiner, J. Jeong, K. C. Rule, M. D. Le, and J.-G. Park, Magnon-phonon coupling and two-magnon continuum in the two-dimensional triangular antiferromagnet CuCrO_2 , *Phys. Rev. B* **94**, 104421 (2016).
 - [18] Y. Oohara, S. Mitsuda, H. Yoshizawa, N. Yaguchi, H. Kuriyama, T. Asano, and M. Mekata, Magnetic phase transition in AgCrO_2 , *J. Phys. Soc. Jpn.* **63**, 847 (1994).
 - [19] A. M. L. Lopes, G. N. P. Oliveira, T. M. Mendonça, J. A. Moreira, A. Almeida, J. P. Araújo, V. S. Amaral, and J. G. Correia, Local distortions in multiferroic AgCrO_2 triangular spin lattice, *Phys. Rev. B* **84**, 014434 (2011).
 - [20] T. Kurumaji, Spiral spin structures and skyrmions in multiferroics, *Phys. Sci. Rev.* **5**, 20190016 (2020).
 - [21] H. Katsura, N. Nagaosa, and A. V. Balatsky, Spin current and magnetoelectric effect in noncollinear magnets, *Phys. Rev. Lett.* **95**, 057205 (2005).
 - [22] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Magnetic control of ferroelectric polarization, *Nature (London)* **426**, 55 (2003).
 - [23] H. J. Xiang, S.-H. Wei, M.-H. Whangbo, and J. L. F. Da Silva, Spin-orbit coupling and ion displacements in multiferroic TbMnO_3 , *Phys. Rev. Lett.* **101**, 037209 (2008).
 - [24] K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa, and T. Arima, Ferroelectric polarization flop in a frustrated magnet MnWO_4 induced by a magnetic field, *Phys. Rev. Lett.* **97**, 097203 (2006).
 - [25] S. Seki, Y. Onose, and Y. Tokura, Spin-driven ferroelectricity in triangular lattice antiferromagnets ACrO_2 ($A = \text{Cu, Ag, Li, or Na}$), *Phys. Rev. Lett.* **101**, 067204 (2008).

- [26] T.-h. Arima, Ferroelectricity induced by proper-screw type magnetic order, *J. Phys. Soc. Jpn.* **76**, 073702 (2007).
- [27] X. Wu, Y. Cai, Q. Xie, H. Weng, H. Fan, and J. Hu, Magnetic ordering and multiferroicity in MnI_2 , *Phys. Rev. B* **86**, 134413 (2012).
- [28] Y. Tokura and S. Seki, Multiferroics with spiral spin orders, *Adv. Mater.* **22**, 1554 (2010).
- [29] H. J. Xiang, E. J. Kan, Y. Zhang, M.-H. Whangbo, and X. G. Gong, General theory for the ferroelectric polarization induced by spin-spiral order, *Phys. Rev. Lett.* **107**, 157202 (2011).
- [30] I. V. Solovyev, Superexchange theory of electronic polarization driven by relativistic spin-orbit interaction at half filling, *Phys. Rev. B* **95**, 214406 (2017).
- [31] J. H. Yang, Z. L. Li, X. Z. Lu, M.-H. Whangbo, S.-H. Wei, X. G. Gong, and H. J. Xiang, Strong Dzyaloshinskii-Moriya interaction and origin of ferroelectricity in Cu_2OSeO_3 , *Phys. Rev. Lett.* **109**, 107203 (2012).
- [32] Y. S. Chai, S. H. Chun, J. Z. Cong, and K. H. Kim, Magnetoelectricity in multiferroic hexaferrites as understood by crystal symmetry analyses, *Phys. Rev. B* **98**, 104416 (2018).
- [33] A. Edström, P. Barone, S. Picozzi, and M. Stengel, Magnetoelectricity of topological solitons in 2D magnets, *npj Comput. Mater.* **11**, 295 (2025).
- [34] S. A. Nikolaev and I. V. Solovyev, Microscopic theory of electric polarization induced by skyrmionic order in GaV_4S_8 , *Phys. Rev. B* **99**, 100401(R) (2019).
- [35] I. Solovyev, R. Ono, and S. Nikolaev, Magnetically induced polarization in centrosymmetric bonds, *Phys. Rev. Lett.* **127**, 187601 (2021).
- [36] I. A. Sergienko and E. Dagotto, Role of the Dzyaloshinskii-Moriya interaction in multiferroic perovskites, *Phys. Rev. B* **73**, 094434 (2006).
- [37] H. J. Xiang, P. S. Wang, M.-H. Whangbo, and X. G. Gong, Unified model of ferroelectricity induced by spin order, *Phys. Rev. B* **88**, 054404 (2013).
- [38] J. Iniguez, First-principles approach to lattice-mediated magnetoelectric effects, *Phys. Rev. Lett.* **101**, 117201 (2008).
- [39] M. Ye and D. Vanderbilt, Dynamical magnetic charges and linear magnetoelectricity, *Phys. Rev. B* **89**, 064301 (2014).
- [40] S. Mankovsky, S. Polesya, H. Lange, M. Weißenhofer, U. Nowak, and H. Ebert, Angular momentum transfer via relativistic spin-lattice coupling from first principles, *Phys. Rev. Lett.* **129**, 067202 (2022).
- [41] S. Mankovsky, H. Lange, S. Polesya, and H. Ebert, Spin-lattice interaction parameters from first principles: Theory and implementation, *Phys. Rev. B* **107**, 144428 (2023).
- [42] K.-I. Gondaira and Y. Tanabe, A note on the theory of superexchange interaction, *J. Phys. Soc. Jpn.* **21**, 1527 (1966).
- [43] D. Vanderbilt and R. D. King-Smith, Electric polarization as a bulk quantity and its relation to surface charge, *Phys. Rev. B* **48**, 4442 (1993).
- [44] R. D. King-Smith and D. Vanderbilt, Theory of polarization of crystalline solids, *Phys. Rev. B* **47**, 1651(R) (1993).
- [45] R. Resta, Macroscopic electric polarization as a geometric quantum phase, *Europhys. Lett.* **22**, 133 (1993).
- [46] C. Jia, S. Onoda, N. Nagaosa, and J. H. Han, Bond electronic polarization induced by spin, *Phys. Rev. B* **74**, 224444 (2006).
- [47] M. E. Rose, *Relativistic Electron Theory* (Wiley, New York, 1961).
- [48] A. H. MacDonald and S. H. Vosko, A relativistic density functional formalism, *J. Phys. C: Solid State Phys.* **12**, 2977 (1979).
- [49] E. Engel and R. M. Dreizler, *Density Functional Theory – An Advanced Course* (Springer, Berlin, 2011).
- [50] H. Ebert, J. Braun, D. Ködderitzsch, and S. Mankovsky, Fully relativistic multiple scattering calculations for general potentials, *Phys. Rev. B* **93**, 075145 (2016).
- [51] T. Moriya, Theory of absorption and scattering of light by magnetic crystals, *J. Appl. Phys.* **39**, 1042 (1968).
- [52] S. Angelov and J. Doumerc, On the correlation between the structure and the exchange interactions in ACrO_2 chromites, *Solid State Commun.* **77**, 213 (1991).
- [53] I. I. Mazin, Electronic structure and magnetism in the frustrated antiferromagnet LiCrO_2 : First-principles calculations, *Phys. Rev. B* **75**, 094407 (2007).
- [54] A. V. Ushakov, D. A. Kukusta, A. N. Yaresko, and D. I. Khomskii, Magnetism of layered chromium sulfides MCrS_2 ($M = \text{Li, Na, K, Ag, and Au}$): A first-principles study, *Phys. Rev. B* **87**, 014418 (2013).
- [55] H. Ebert *et al.*, The Munich SPR-KKR package, version 8.5 (2020), <https://www.ebert.cup.uni-muenchen.de/en/software-en/13-sprkk/>.
- [56] H. Ebert, D. Ködderitzsch, and J. Minar, Calculating condensed matter properties using the KKR-Green's function method – Recent developments and applications, *Rep. Prog. Phys.* **74**, 096501 (2011).
- [57] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [58] S. Mankovsky, S. Polesya, and H. Ebert, Extension of the standard Heisenberg Hamiltonian to multispin exchange interactions, *Phys. Rev. B* **101**, 174401 (2020).
- [59] T. Sato, H. Kadowaki, and K. Iio, Successive phase transitions in the hexagonal-layered Heisenberg antiferromagnets MnX_2 ($X = \text{Br, I}$), *Physica B* **213-214**, 224 (1995).
- [60] T. Kurumaji, S. Seki, S. Ishiwata, H. Murakawa, Y. Tokunaga, Y. Kaneko, and Y. Tokura, Magnetic-field induced competition of two multiferroic orders in a triangular-lattice helimagnet MnI_2 , *Phys. Rev. Lett.* **106**, 167206 (2011).
- [61] F. Ye, Y. Ren, Q. Huang, J. A. Fernandez-Baca, P. Dai, J. W. Lynn, and T. Kimura, Spontaneous spin-lattice coupling in the geometrically frustrated triangular lattice antiferromagnet CuFeO_2 , *Phys. Rev. B* **73**, 220404(R) (2006).
- [62] H. Kadowaki, H. Kikuchi, and Y. Ajiro, Neutron powder diffraction study of the two-dimensional triangular lattice antiferromagnet CuCrO_2 , *J. Phys.: Condens. Matter* **2**, 4485 (1990).
- [63] M. Poienar, F. Damay, C. Martin, V. Hardy, A. Maignan, and G. André, Structural and magnetic properties of $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ by neutron powder diffraction, *Phys. Rev. B* **79**, 014412 (2009).
- [64] M. Soda, K. Kimura, T. Kimura, M. Matsuura, and K. Hirota, Electric control of spin helicity in multiferroic triangular lattice antiferromagnet CuCrO_2 with proper-screw order, *J. Phys. Soc. Jpn.* **78**, 124703 (2009).
- [65] K. Kimura, T. Otani, H. Nakamura, Y. Wakabayashi, and T. Kimura, Lattice distortion coupled with magnetic ordering in a triangular lattice antiferromagnet CuCrO_2 , *J. Phys. Soc. Jpn.* **78**, 113710 (2009).
- [66] K. Kimura, H. Nakamura, K. Ohgushi, and T. Kimura, Magnetoelectric control of spin-chiral ferroelectric domains in a triangular lattice antiferromagnet, *Phys. Rev. B* **78**, 140401(R) (2008).

- [67] K. Kimura, H. Nakamura, S. Kimura, M. Hagiwara, and T. Kimura, Tuning ferroelectric polarization reversal by electric and magnetic fields in CuCrO_2 , *Phys. Rev. Lett.* **103**, 107201 (2009).
- [68] E. Mun, M. Frontzek, A. Podlesnyak, G. Ehlers, S. Barilo, S. V. Shiryayev, and V. S. Zapf, High magnetic field evolution of ferroelectricity in CuCrO_2 , *Phys. Rev. B* **89**, 054411 (2014).
- [69] See Supplemental Material at <https://link.aps.org/supplemental/10.1103/9fs1-5gxq> for additional details on the calculations concerning the spin-order induced polarization in MnI_2 (Sec. A) and in Cr_2O_3 (Sec. B) and it presents a number of additional applications of the scheme presented in the manuscript, to illustrate the wide range of materials and issues that can be addressed by it, which includes Ref. [76].
- [70] I. Dzyaloshinskii, On the magneto-electrical effect in antiferromagnets, *Sov. Phys.-JETP* **10**, 628 (1960).
- [71] E. Kita, K. Siratori, and A. Tasaki, Experimental determination of the mechanism of ME effect of Cr_2O_3 from ME susceptibility and electric shift in the antiferromagnetic resonance, *J. Appl. Phys.* **50**, 7748 (1979).
- [72] E. Bousquet, N. A. Spaldin, and K. T. Delaney, Unexpectedly large electronic contribution to linear magnetoelectricity, *Phys. Rev. Lett.* **106**, 107202 (2011).
- [73] P. J. Brown, J. B. Forsyth, E. Lelièvre-Berna, and F. Tasset, Determination of the magnetization distribution in Cr_2O_3 using spherical neutron polarimetry, *J. Phys.: Condens. Matter* **14**, 1957 (2002).
- [74] A. Scaramucci, E. Bousquet, M. Fechner, M. Mostovoy, and N. A. Spaldin, Linear magnetoelectric effect by orbital magnetism, *Phys. Rev. Lett.* **109**, 197203 (2012).
- [75] H. Ebert, S. Mankovsky, K. Chadova, S. Polesya, J. Minár, and D. Ködderitzsch, Calculating linear response functions for finite temperatures on the basis of the alloy analogy model, *Phys. Rev. B* **91**, 165132 (2015).
- [76] A. Yoshimori, A new type of antiferromagnetic structure in the rutile type crystal, *J. Phys. Soc. Jpn.* **14**, 807 (1959).