Magnetically Induced Polarization in Centrosymmetric Bonds

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We reveal the microscopic origin of electric polarization $\vec{P}$ induced by noncollinear magnetic order. We show that in Mott insulators, such $\vec{P}$ is given by all possible combinations of position operators $\hat{\vec{r}}_{ij} = (\vec{r}^0_{ij}, \vec{\boldsymbol{r}}_{ij})$ and transfer integrals $\hat{t}_{ij} = (t^0_{ij}, \boldsymbol{t}_{ij})$ in the bonds, where $\vec{r}^0_{ij}$ and t^0_{ij} are spin-independent contributions in the basis of Kramers doublet states, while $\vec{\boldsymbol{r}}_{ij}$ and $\boldsymbol{t}_{ij}$ stem solely from the spin-orbit interaction. Among them, the combination $t^0_{ij}\vec{\boldsymbol{r}}_{ij}$, which couples to the spin current, remains finite in the centrosymmetric bonds, thus yielding finite $\vec{P}$ in the case of noncollinear arrangement of spins. The form of the magnetoelectric coupling, which is controlled by $\vec{\boldsymbol{r}}_{ij}$, appears to be rich and is not limited to the phenomenological law $\vec{P} \sim \boldsymbol{\epsilon}_{ij} \times [\boldsymbol{e}_i \times \boldsymbol{e}_j]$ with $\boldsymbol{\epsilon}_{ij}$ being the bond vector connecting the spins $\boldsymbol{e}_i$ and $\boldsymbol{e}_j$. Using density-functional theory, we illustrate how the proposed mechanism works in the spiral magnets $CuCl_2$, $CuBr_2$, CuO, and α-Li_2IrO_3, providing a consistent explanation for the available experimental data.

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Introduction.—In order to make a material ferroelectric, it is essential to break the inversion symmetry. Canonically, this implies some crystallographic instability toward polar atomic displacements [1]. Nevertheless, there is a very special class of materials, called multiferroics, where inversion symmetry can be broken by magnetic means in an otherwise perfect crystallographically centrosymmetric lattice [2]. The microscopic origin of multiferroicity is the fundamental physical problem and its practical realization is an important step toward mutual control of electric polarization and magnetism in novel electronic devices.

There can be various scenarios of the magnetic inversion symmetry breaking. In certain multiferroic materials, the inversion symmetry is microscopically broken by local distortions, so that individual bonds can be formally associated with some polarization vectors. When arranged in an antiferroelectric manner, these bonds result in zero net polarization. Nevertheless, if some of them become inequivalent owing to complex magnetic order, the perfect cancellation of polarization vectors does not occur and the system becomes ferroelectric.

However, what if the bond itself is centrosymmetric? Can it become electrically polarized by magnetic means? An affirmative answer to these questions was given by Katsura, Nagaosa, and Balatsky (KNB) [3], who considered a very special microscopic model and argued that the noncollinear alignment of spins can induce the polarization $\vec{P} \sim \boldsymbol{\epsilon}_{ij} \times [\boldsymbol{e}_i \times \boldsymbol{e}_j]$, which lies in the plane of spins $\boldsymbol{e}_i$ and $\boldsymbol{e}_j$ and is perpendicular to the bond vector $\boldsymbol{\epsilon}_{ij}$. This finding was supported by phenomenological considerations [4], and the proposed mechanism was called the "spin-current mechanism," which is widely used for the analysis of magnetoelectric coupling in spiral magnets [5], typically in combination with two other mechanisms: "exchange striction" [6,7] and "spin-dependent p-d hybridization" [8].

Nevertheless, the analysis remains largely phenomenological. First, the properties of all spiral multiferroics are usually discussed from the viewpoint of the spin-current model [9–14]. However, there are only few materials, such as $CuCl_2$ [9] and $CuBr_2$ [10], consisting solely of the centrosymmetric bonds. In other materials, the situation is not so straightforward [11–14]: as the symmetry is low, the bonds are not necessarily centrosymmetric, thus allowing for alternative explanations [15–17]. Then, if the KNB model fails to explain the properties of spiral magnets, it typically causes some confusion with identifying the problem and choosing a suitable alternative [18]. Although density-functional theory (DFT) provides a powerful tool for calculating the polarization [19,20], the formal mapping of DFT results on a specifically selected model [21] does not shed light on microscopic mechanisms underlying this model.

In this Letter, we formulate a transparent microscopic theory of electric polarization induced by noncollinear magnetic order. We explicitly show how and why the noncollinear arrangement of spins gives rise to electric polarization even in centrosymmetric bonds. We relate the magnetoelectric coupling to fundamental symmetry properties of the position operator and transfer integrals in the basis of Kramers states and argue that the paradigm of the spin current–induced polarization appears to be much richer and goes beyond the phenomenological low $\vec{P} \sim \boldsymbol{e}_{ij} \times [\boldsymbol{e}_i \times \boldsymbol{e}_j]$ [17,18,21]. We evaluate all relevant parameters on the basis of DFT and show how they are manifested in the properties of real spiral magnets.

Basic theory.—The simplest toy model, which captures the physics, is the 1-orbital Hubbard model with spin-orbit interaction (SOI):

$$\hat{\mathcal{H}} = \sum_{ij}\sum_{\sigma\sigma'} t_{ij}^{\sigma\sigma'} \hat{c}_{i\sigma}^{\dagger}\hat{c}_{j\sigma'} + U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}, \tag{1}$$

where $\hat{c}_{i\sigma}^{\dagger}$ ($\hat{c}_{i\sigma}$) creates (annihilates) a hole with pseudospin $\sigma = +$ or $-$ at site i, $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^{\dagger}\hat{c}_{i\sigma}$ and $\hat{t}_{ij} = [t_{ij}^{\sigma\sigma'}]$ are the transfer integrals, and U is the on-site Coulomb repulsion. The Wannier functions, $|i\sigma\rangle = \hat{c}_{i\sigma}^{\dagger}|0\rangle$, can be chosen as the Kramers pairs, transforming under the time reversal as $\hat{T}|i\mp\rangle = \pm|i\pm\rangle$. All model parameters are derived from DFT [22] in the subspace of Wannier states, which are primarily responsible for the magnetism [20,23]. The Coulomb U is evaluated within constrained random-phase approximation [24].

Since the polarization in metals is screened by free electrons, the multiferroicity is the property of insulating state. Then, the problem can be solved in the spirit of superexchange theory by treating $\hat{t}_{ij}$ as a perturbation [25]. Let $|\alpha_i^o\rangle = \cos(\theta_i/2)|i+\rangle - \sin(\theta_i/2)e^{-i\phi_i}|i-\rangle$ be the occupied orbital in the limit $\hat{t}_{ij} = 0$, where θ_i and ϕ_i specify the direction $\boldsymbol{e}_i = (\cos\phi_i \sin\theta_i, \sin\phi_i \sin\theta_i, \cos\theta_i)$ of spin, and $|\alpha_i^u\rangle = \sin(\theta_i/2)e^{i\phi_i}|i+\rangle + \cos(\theta_i/2)|i-\rangle$ is the unoccupied orbital. To the first order in $(\hat{t}_{ij}/U)$, $|\alpha_i^o\rangle$ will transform to the Wannier function $|w_i\rangle = |\alpha_i^o\rangle + \sum_j |\alpha_{i\to j}^o\rangle$, acquiring the tails

$$|\alpha_{i\to j}^o\rangle = -\frac{1}{U}|\alpha_j^u\rangle\langle\alpha_j^u|\hat{t}_{ji}|\alpha_i^o\rangle \tag{2}$$

on surrounding sites j. Considering expectation values of the kinetic energy $\langle w_i|\hat{t}_{ij}|w_i\rangle$, one can readily formulate the spin model

$$\mathcal{E} = \sum_{\langle ij\rangle}(-J_{ij}\boldsymbol{e}_i\cdot\boldsymbol{e}_j + \boldsymbol{D}_{ij}\cdot[\boldsymbol{e}_i\times\boldsymbol{e}_j] + \boldsymbol{e}_i\cdot\overleftrightarrow{\Gamma}_{ij}\boldsymbol{e}_j), \tag{3}$$

describing the energy change in terms of isotropic (J_{ij}), Dzyaloshinskii-Moriya (DM, $\boldsymbol{D}_{ij}$), and symmetric anisotropic ($\overleftrightarrow{\Gamma}_{ij}$) interactions. A similar model can be formulated for polarization [26]:

$$\vec{P} = \sum_{\langle ij\rangle}(\vec{\mathsf{P}}_{ij}\boldsymbol{e}_i\cdot\boldsymbol{e}_j + \vec{\boldsymbol{\mathcal{P}}}_{ij}\cdot[\boldsymbol{e}_i\times\boldsymbol{e}_j] + \boldsymbol{e}_i\cdot\vec{\boldsymbol{\Pi}}_{ij}\boldsymbol{e}_j), \tag{4}$$

in terms of the vector $\vec{\mathsf{P}}_{ij} \equiv [\mathsf{P}_{ij}^{v}]$, rank-2 tensor $\vec{\boldsymbol{\mathcal{P}}}_{ij} \equiv [\mathcal{P}_{ij}^{v,c}]$, and rank-3 tensor $\vec{\boldsymbol{\Pi}}_{ij} \equiv [\Pi_{ij}^{v,ab}]$ [27]. The model parameters can be obtained from matrix elements of the position operator in the framework of general theory for polarization in periodic systems [19,20]:

$$\vec{P} = -\frac{e}{V}\sum_i \langle w_i|\vec{r}|w_i\rangle \tag{5}$$

(where V is the volume and $-e$ is the electron charge). Then, the only matrix elements that contribute to the magnetic dependence of $\vec{P}$ are of the type $\langle\alpha_i^o|\vec{r}|\alpha_{i\to j}^o\rangle$. Other contributions, such as $\langle\alpha_{i\to j}^o|\vec{r}|\alpha_{i\to j}^o\rangle$ or single-ion anisotropy of $\vec{P}$, vanish in the 1-orbital model [17,18].

The 2×2 matrices $\hat{t}_{ij}$ and $\hat{\vec{r}}_{ij}$ can be decomposed in terms of the unity $\hat{\mathbb{1}}$ and the vector $\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$ of Pauli matrices as $\hat{t}_{ij} = t_{ij}^0\hat{\mathbb{1}} + i\boldsymbol{t}_{ij}\hat{\boldsymbol{\sigma}}$ and $\hat{\vec{r}}_{ij} = \vec{r}_{ij}^{\,0}\hat{\mathbb{1}} + i\vec{\boldsymbol{r}}_{ij}\hat{\boldsymbol{\sigma}}$ with the real coefficients $(t_{ij}^0, \boldsymbol{t}_{ij})$ and $(\vec{r}_{ij}^{\,0}, \vec{\boldsymbol{r}}_{ij})$. Furthermore, the hermiticity yields $t_{ji}^0 = t_{ij}^0$, $\boldsymbol{t}_{ji} = -\boldsymbol{t}_{ij}$, $\vec{r}_{ji}^{\,0} = \vec{r}_{ij}^{\,0}$, and $\vec{\boldsymbol{r}}_{ji} = -\vec{\boldsymbol{r}}_{ij}$ [28]. The corresponding spin model parameters are summarized in Table I [29].

A very special case is when two sites i and j are connected by spacial inversion. Since $\hat{t}_{ij}$ is a scalar but $\hat{\vec{r}}_{ij}$ is a (true) vector, inversion symmetry requires that $\hat{t}_{ji} = \hat{t}_{ij}$ but $\hat{\vec{r}}_{ji} = -\hat{\vec{r}}_{ij}$. In combination with hermiticity, we have $\boldsymbol{t}_{ij} = 0$ and $\vec{r}_{ij}^{\,0} = 0$. Then, the DM interaction $\boldsymbol{D}_{ij}$ vanishes, which is the general property of centrosymmetric ($\subset$) bonds, and so does $\boldsymbol{\Gamma}_{ij}$, being not independent in the 1-orbital model [31]. Thus, the only interaction in the $\subset$ bonds will be J_{ij}. The behavior of electric polarization is different: $\vec{\mathsf{P}}_{ij} = 0$ and $\vec{\boldsymbol{\Pi}}_{ij} = 0$, while $\vec{\mathsf{P}}_{ij} = -(2e/V)(t_{ij}^0\vec{\boldsymbol{r}}_{ij}/U) \equiv \vec{\boldsymbol{\mathcal{C}}}_{ij}$ can persist even in the $\subset$ bond

TABLE I. Isotropic (J_{ij} and $\vec{\mathsf{P}}_{ij}$), antisymmetric ($\boldsymbol{D}_{ij}$ and $\vec{\boldsymbol{\mathcal{P}}}_{ij}$), and anisotropic symmetric ($\boldsymbol{\Gamma}_{ij} = \boldsymbol{\Gamma}'_{ij} - \frac{1}{2}\mathrm{Tr}\boldsymbol{\Gamma}'_{ij}$ and $\vec{\boldsymbol{\Pi}}_{ij} = \vec{\boldsymbol{\Pi}}'_{ij} - \frac{1}{2}\mathrm{Tr}\vec{\boldsymbol{\Pi}}'_{ij}$) parameters of exchange interactions and polarization. $\otimes$ denotes the direct product.

Exchange	Polarization
$J_{ij} = -[(t_{ij}^0)^2/U]$	$\vec{\mathsf{P}}_{ij} = -(2e/V)(\vec{r}_{ij}^{\,0}t_{ij}^0/U)$
$\boldsymbol{D}_{ij} = (2t_{ij}^0\boldsymbol{t}_{ij}/U)$	$\vec{\boldsymbol{\mathcal{P}}}_{ij} = -(2e/V)[(\vec{r}_{ij}^{\,0}\boldsymbol{t}_{ij} + t_{ij}^0\vec{\boldsymbol{r}}_{ij})/U]$
$\boldsymbol{\Gamma}'_{ij} = [(2\boldsymbol{t}_{ij}\otimes\boldsymbol{t}_{ij})/U]$	$\vec{\boldsymbol{\Pi}}'_{ij} = -(e/V)[(\vec{\boldsymbol{r}}_{ij}\otimes\boldsymbol{t}_{ij} + \boldsymbol{t}_{ij}\otimes\vec{\boldsymbol{r}}_{ij})/U]$

(in agreement with symmetry arguments [21]), and the corresponding polarization $\vec{\mathcal{C}}_{ij}\cdot[\boldsymbol{e}_i\times\boldsymbol{e}_j]$ is induced solely by the noncollinear arrangement of spins.

In the noncentrosymmetric (nc) bonds, $\boldsymbol{t}_{ij}$ and $\vec{r}^{\,0}_{ij}$ are finite, resulting in nonzero $\boldsymbol{D}_{ij}$, $\boldsymbol{\Gamma}_{ij}$, $\vec{\mathsf{P}}_{ij}$, and $\vec{\boldsymbol{\Pi}}_{ij}$. Moreover, $\vec{\mathcal{P}}_{ij}$ acquires an additional asymmetric contribution $\vec{\mathcal{A}}_{ij}=-(2e/V)(\vec{r}^{\,0}_{ij}\boldsymbol{t}_{ij}/U)$. $\vec{\mathsf{P}}_{ij}$ and $\vec{\mathcal{A}}_{ij}$ can be viewed as a regular polarization of the nc bond, $-(e\vec{r}^{\,0}_{ij}/V)$, which is additionally modulated by the spin texture. If this texture results from the competition of $\boldsymbol{D}_{ij}$ and J_{ij}, a similar competition takes place between $\vec{\mathcal{A}}_{ij}$ and $\vec{\mathsf{P}}_{ij}$, as it depends on the same ratio $(\boldsymbol{t}_{ij}/t^0_{ij})$. Therefore, there will be a cancellation of contributions associated with $\vec{\mathcal{A}}_{ij}$ and $\vec{\mathsf{P}}_{ij}$ [18].

The 1-orbital model is subjected to hidden symmetries that allow the full elimination of $\boldsymbol{t}_{ij}$ by rotating the spins at sites i and j [31]. In such local coordinate frame, the bond is solely described by the transfer integral $\tilde{t}^0_{ij}=\sqrt{(t^0_{ij})^2+\boldsymbol{t}_{ij}\cdot\boldsymbol{t}_{ij}}$, the exchange interactions are described by J_{ij}, and the electric polarization is described by the competition of $\vec{\mathsf{P}}_{ij}$ and $\vec{\mathcal{C}}_{ij}$ (with $\tilde{t}^0_{ij}$ instead of t^0_{ij}). Using $|\alpha^u_j\rangle\langle\alpha^u_j|=\hat{\mathbb{1}}-|\alpha^o_j\rangle\langle\alpha^o_j|$ in Eq. (2), each term in the spin model can be further expressed via the expectation value of some quantity in the ground state. Since $[\boldsymbol{e}_i\times\boldsymbol{e}_j]$ is related to the spin current $\hat{\boldsymbol{j}}^s_{ij}=(i\tilde{t}^0_{ij}/2)(\hat{\tilde{c}}^\dagger_{i\sigma}\hat{\boldsymbol{\sigma}}_{\sigma\sigma'}\hat{\tilde{c}}_{j\sigma'}-\hat{\tilde{c}}^\dagger_{j\sigma}\hat{\boldsymbol{\sigma}}_{\sigma\sigma'}\hat{\tilde{c}}_{i\sigma'})$ [32], one can find that $\vec{P}\sim\vec{\mathcal{C}}_{ij}\cdot\langle\hat{\boldsymbol{j}}^S_{ij}\rangle$ [29] in analogy with the DM interactions [33].

The 3×3 tensor $\vec{\mathcal{C}}_{ij}=[\mathcal{C}^{v,c}_{ij}]$ can be generally decomposed into symmetric and antisymmetric parts, $\vec{\mathcal{C}}_{ij}=\vec{\mathcal{C}}^S_{ij}+\vec{\mathcal{C}}^A_{ij}$. The latter is expressed as $\varepsilon_{vca}\boldsymbol{\pi}^a_{ij}$, in terms of the vector $\boldsymbol{\pi}_{ij}=[\pi^a_{ij}]$ and Levi-Civita symbol ε_{vca}. The corresponding $\vec{P}=\boldsymbol{\pi}_{ij}\times[\boldsymbol{e}_i\times\boldsymbol{e}_j]$ is reminiscent of the KNB expression [3,4]. Nevertheless, $\boldsymbol{\pi}_{ij}$ is not necessarily parallel to $\boldsymbol{\epsilon}_{ij}$, and $\vec{\mathcal{C}}$ can include $\vec{\mathcal{C}}^S_{ij}$. Thus, the proposed spin-current theory is not limited to the conventional law $\vec{P}\sim\boldsymbol{\epsilon}_{ij}\times[\boldsymbol{e}_i\times\boldsymbol{e}_j]$ and includes other interesting options. Below, we consider examples of how it works for different symmetries.

Relativistic $j=\frac{1}{2}$ manifold of t_{2g} states.—In the cubic environment, the sixfold degenerate t_{2g} states are split by SOI into fourfold degenerate Γ_8 states and the Kramers pair of Γ_7 states $|+\rangle=(1/\sqrt{3})(|xy\downarrow\rangle-|yz\uparrow\rangle+i|zx\uparrow\rangle)$ and $|-\rangle=(1/\sqrt{3})(|xy\uparrow\rangle+|yz\downarrow\rangle+i|zx\downarrow\rangle)$. The latter can be viewed as the effective $j=\frac{1}{2}$ pseudospin states, which play a key role in the physics of spin-orbit Mott insulators realized in $5d$ Ir oxides [34]. Since the KNB expression was derived assuming this symmetry of states [3], we start our analysis with this example and consider a perfect bond obeying the C^z_∞ symmetry along z. It is straightforward to show that the only nonzero elements of $\vec{\boldsymbol{r}}_{ij}=[r^{v,c}_{ij}]$ will be $r^{y,x}_{ij}=-r^{x,y}_{ij}=\frac{1}{3}(\langle xy_i|y|zx_j\rangle-\langle zx_i|y|xy_j\rangle)$ [29]. The antisymmetric tensor can be presented as $\varepsilon_{abz}\pi^z_{ij}$, where $ab=xy$ or yx, and the vector $\boldsymbol{\pi}_{ij}=(0,0,\pi^z_{ij})$ is indeed parallel to the bond. Thus, we do recover the KNB expression $\vec{P}\sim\boldsymbol{\epsilon}_{ij}\times[\boldsymbol{e}_i\times\boldsymbol{e}_j]$ [3]. Nevertheless, this form of $\vec{P}$ is the consequence of the particular symmetry of undistorted t_{2g} states. Other symmetries may yield different $\vec{P}$.

z^2 states with SOI.—The simplest example illustrating this idea is the z^2 states, which are stabilized by the crystal field and mixed with the yz and zx states by SOI. The Kramers states are [35] $|+\rangle\propto|z^2\downarrow\rangle+\xi(i|yz\uparrow\rangle-|zx\uparrow\rangle)$ and $|-\rangle\propto|z^2\uparrow\rangle+\xi(i|yz\downarrow\rangle+|zx\downarrow\rangle)$ (ξ being the ratio of SOI to the crystal field splitting), and the nonvanishing elements $r^{v,c}_{ij}$ are $r^{y,x}_{ij}=r^{x,y}_{ij}\propto\langle z^2_i|x|zx_j\rangle-\langle zx_i|x|z^2_j\rangle$ [29]. Thus, the tensor $[r^{v,c}_{ij}]$ is symmetric, meaning that for two noncollinear spins $\boldsymbol{e}_{1,2}=(\sin\theta\cos\varphi,\sin\theta\sin\varphi,\pm\cos\theta)$, the polarization $\vec{P}\sim(\cos\varphi,-\sin\varphi,0)$ is still perpendicular to the bond but does not necessarily lie in the spin plane.

α-Li_2IrO_3.—As the first realistic example, it is instructive to consider the spin-orbit Mott insulator α-Li_2IrO_3, which attracted a great deal of attention as a possible material for realizing the Kitaev spin liquid state [36]. In this monoclinic compound (space group $C2/m$), there are two types of nearest c bonds: the strongest one [01 in Fig. 1(a)] along the monoclinic b axis, which is transformed to itself by the twofold rotation about b, and two rotationally noninvariant weak bonds (02 and 03) that are connected by the twofold rotation.

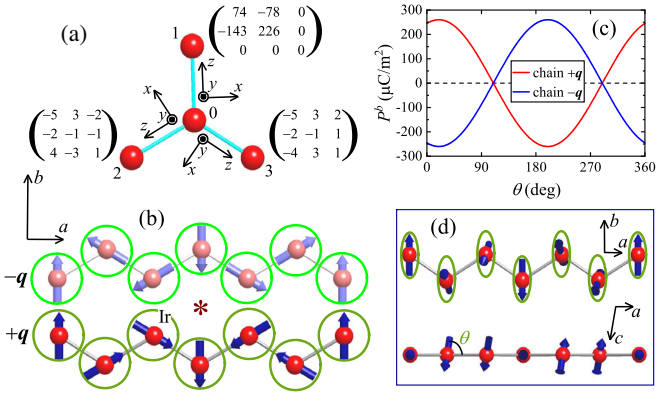

FIG. 1. (a) Tensor $\vec{\mathcal{C}}_{ij}$ in the nearest c bonds of α-Li_2IrO_3 (in $\mu C/m^2$) in the local coordinate frames denoted by x, y, and z. (b) Double-$\boldsymbol{q}$ magnetic structure realized in α-Li_2IrO_3. Inversion center is denoted by $*$. (c) Magnetically induced polarization in the chains with $+\boldsymbol{q}$ and $-\boldsymbol{q}$ depending on the rotation of the spin-spiral plane about the monoclinic b axis, as explained in (d) in the planes ab and bc. θ is the angle formed by the spin-spiral plane and the monoclinic a axis.

The minimal model was constructed for the magnetic $j = \frac{1}{2}$ bands [29]. In the local coordinate frame, where the z axis is along the bond, the tensor $\vec{\mathcal{C}}_{01}$ has only x and y components [see Fig. 1(a)]. Hence, the polarization is perpendicular to the bond and, considering only the antisymmetric part of $\vec{\mathcal{C}}_{01}$, we would indeed obtain $\vec{P} \sim \boldsymbol{\epsilon}_{01} \times [\boldsymbol{e}_0 \times \boldsymbol{e}_1]$ [3,4]. However, besides the antisymmetric contribution, $\vec{\mathcal{C}}_{01}$ clearly shows a strong symmetric one, which is expected for this type of symmetry [37]. In the low-symmetry bonds 02 and 03, $\vec{\mathcal{C}}_{ij}$ is even more complex: all elements are finite and inequivalent, so that the polarization can be perpendicular as well as parallel to the bond.

Since α-Li_2IrO_3 is a noncollinear magnet with $\boldsymbol{q} \approx (\frac{1}{3}, 0, 0)$ [38], it is interesting to ask whether it can become multiferroic. The magnetic texture can be viewed as the double-$\boldsymbol{q}$ spiral, propagating in alternating zigzag chains with $+\boldsymbol{q}$ and $-\boldsymbol{q}$ [Fig. 1(b)]. The spiral order induces an appreciable polarization in each of the chains [Fig. 1(c)]. However, the chains are connected by the inversion operation, the contributions with $+\boldsymbol{q}$ and $-\boldsymbol{q}$ cancel each other, and α-Li_2IrO_3 remains antiferroelectric.

Copper dihalides.—$CuCl_2$ and $CuBr_2$ form the chainlike monoclinic structure (space group $C2/m$), where all Cu-Cu bonds are centrosymmetric. Below the Néel temperature ($T_N = 24$ and 74 K for $CuCl_2$ and $CuBr_2$, respectively), they develop a cycloidal magnetic order with $\boldsymbol{q} \approx (1, \frac{1}{4}, \frac{1}{2})$ [Fig. 2(a)], which coincides with the onset of ferroelectricity [9,10].

The minimal model was constructed for the magnetic "Cu $x^2 - y^2$" bands [29]. The obtained parameters J_{ij} nicely reproduce the experimental cycloidal order [39]. Polarization induced by the cycloidal order is related to $\vec{\mathcal{C}}_{ij}$. Since twofold rotations about b transform the chains to themselves, the symmetry properties of $\vec{\mathcal{C}}_{ij}$ in these chains are similar to $\vec{\mathcal{C}}_{01}$ in α-Li_2IrO_3 [Fig. 1(a)], and the polarization is expected to be perpendicular to b. In the nearest bonds $\pm b$, the antisymmetric part of $\vec{\mathcal{C}}_{\pm b}$ is given by $\boldsymbol{\pi}_{\pm b} = (0, \pm 0.5, 0)$ and $(0, \pm 8, 0)$ μC/m^2 for $CuCl_2$ and $CuBr_2$, respectively, which is too small to account for the total $\vec{P}$, and a substantially larger contribution stems from the symmetric part. The behavior of $\vec{P}$ (after summation over all bonds) is summarized in Figs. 2(d) and (e). For $CuCl_2$, we note a good agreement with the experiment [9], including deviation of $\vec{P}$ from the spin-spiral plane by the angle $\theta + \theta_P$. Similar behavior is expected for $CuBr_2$ with somewhat larger T_N and $\vec{P}$ due to stronger SOI and hybridization mediated by Br $4p$ states.

Cupric oxide.—CuO with the centrosymmetric monoclinic structure (space group $C2/c$) has attracted much attention as a simple binary material that becomes multiferroic at exceptionally high temperature [13].

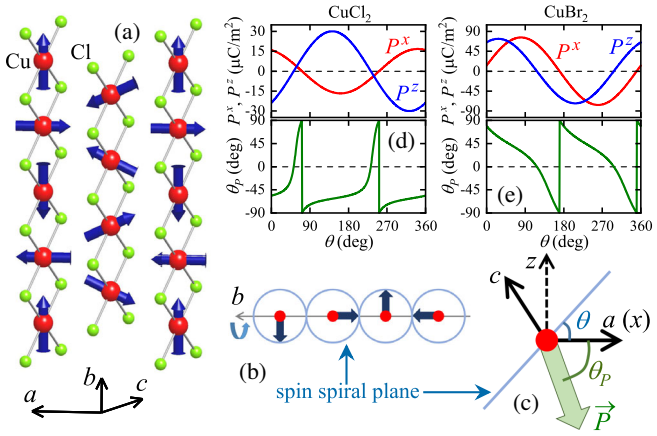

FIG. 2. (a) Crystal and magnetic structure of $CrCl_2$ in the ab plane. (b) Rotations of the spin-spiral plane about the axis b. (c) Angles θ and $\theta_P = \tan^{-1}(P^z/P^x)$ specifying the spiral plane and electric polarization, respectively. (d),(e) Angle dependence of electric polarization in $CuCl_2$ and $CuBr_2$.

Ferroelectricity is driven by a spiral magnetic order with $\boldsymbol{q} \approx (\frac{1}{2}, 0, -\frac{1}{2})$ [see Fig. 3(a)] emerging between 213 and 230 K [40] (and is expected even at room temperature under hydrostatic pressure [41]).

Construction of the minimal model is similar to Cu dihalides [29]. Although the crystal structure of CuO

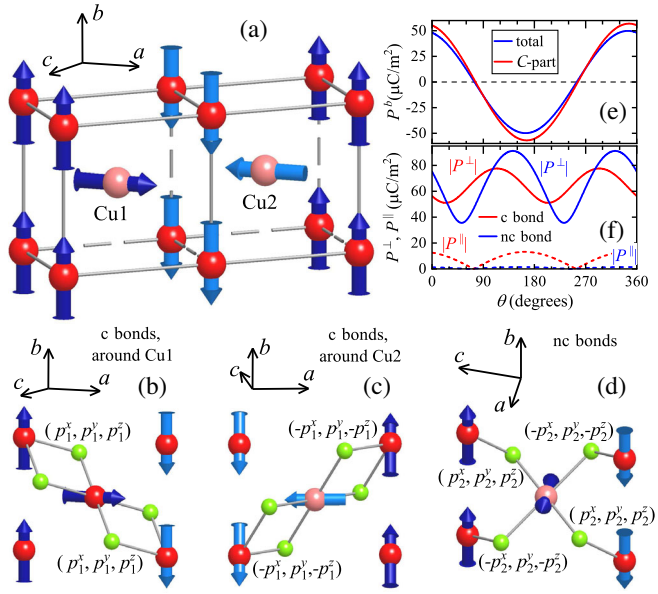

FIG. 3. (a) Spiral magnetic order in CuO. (b),(c) Nearest c and (d) nc bonds in the monoclinic planes ab and bc with the vectors of induced polarization. (e) Electric polarization (total and centrosymmetric part described by $\vec{\mathcal{C}}_{ij}$) as the function of angle θ formed by the spins in the ac plane with the axis a. Here, x and y are chosen along a and b, respectively, and z is perpendicular to a and b. (f) Electric polarization perpendicular ($P^\perp$) and parallel ($P^\parallel$) to the bond, calculated for the nearest c and nc bonds as a function of θ.

includes both c and nc bonds (Fig. 3), the parameters associated with the latter can be largely eliminated [42], while $\vec{\mathcal{C}}_{ij}$ is responsible for 90% of $\vec{P}$ [Fig. 3(e)].

Since the symmetry is low, the form of $\vec{\mathcal{C}}_{ij}$ is complex [29], and the polarization vectors in individual bonds are specified by all three projections, as shown in Fig. 3. Notably, there can be appreciable components along the bonds [Fig. 3(f)]. Nevertheless, due to the twofold rotations about y (b), only the y component of $\vec{P}$ will survive after summation over all equivalent bonds. This is an important point where the symmetry comes into play: the experimental polarization is induced along the y axis, but not because of the phenomenological rule $\boldsymbol{q} \times [\boldsymbol{e}_i \times \boldsymbol{e}_j]$ [3,4]. Quite the contrary, it is a consequence of the particular $C2/c$ symmetry of CuO. Total $P^b \approx 55\ \mu\mathrm{C/m^2}$ is comparable to the experimental $P^b \sim 150\ \mu\mathrm{C/m^2}$ [13,43].

Conclusion.—We have presented a toy theory revealing the fundamental origin of the magnetic inversion symmetry breaking in centrosymmetric systems. Because of the intrinsic symmetries of the transfer integrals and position operator in the basis of Kramers states, the combination $t^0_{ij}\vec{\boldsymbol{r}}_{ij}$ remains finite, yielding finite polarization for noncollinear spins. This polarization depends on the symmetry of Kramers states, providing new alternatives beyond the phenomenological spin-current model. The abilities of the proposed theory are illustrated on spiral magnets $CuCl_2$, $CuBr_2$, CuO, and α-Li_2IrO_3.

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