

Canted-spin-caused electric dipoles: A local symmetry theory

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A pair of magnetic atoms with canted spins $\mathbf{S}_a, \mathbf{S}_b$ can give rise to an electric dipole moment \mathbf{P} . Several forms for the behavior of such a moment have appeared in the theoretical literature, some of which have been invoked to explain experimental results found in various multiferroic materials. The forms that require canting of the spins are $\mathbf{P}_1 \propto \mathbf{R} \times (\mathbf{S}_a \times \mathbf{S}_b)$, $\mathbf{P}_2 \propto \mathbf{S}_a \times \mathbf{S}_b$, and $\mathbf{P}_3 \propto \mathbf{S}_a \mathbf{R} \cdot \mathbf{S}_a - \mathbf{S}_b \mathbf{R} \cdot \mathbf{S}_b$, where \mathbf{R} is the relative position of the atoms and $\mathbf{S}_a, \mathbf{S}_b$ are unit vectors. To unify and generalize these various forms, we consider \mathbf{P} as the most general quadratic function of the spin components that vanishes whenever \mathbf{S}_a and \mathbf{S}_b are collinear, i.e., we consider the most general expressions that require spin canting. The study reveals new forms. We generalize to the vector \mathbf{P} , Moriya's symmetry considerations regarding the (scalar) Dzyaloshinskii-Moriya energy $\mathbf{D} \cdot \mathbf{S}_a \times \mathbf{S}_b$ (which led to restrictions on \mathbf{D}). This provides a rigorous symmetry argument that shows that \mathbf{P}_1 is allowed no matter how high the symmetry of the atoms plus environment, and gives restrictions for all other contributions. The analysis leads to the suggestion of terms omitted in the existing microscopic models, suggests a new mechanism behind the ferroelectricity found in the "proper screw structure" of CuXO_2 , $X = \text{Fe, Cr}$, and predicts an unusual antiferroelectric ordering in the antiferromagnetically and ferroelectrically ordered phase of $\text{RbFe}(\text{MoO}_4)_2$.

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I. INTRODUCTION

The great deal of recent interest in multiferroic materials,¹⁻³⁴ in which magnetic ordering of various sorts induces ferro- or ferrielectricity, forces one to understand the microscopic foundation for this surprising, and possibly useful, effect. Broadly, there are two sources of this fascinating effect. One, found in many materials, depends on the canting of the spins in an essential way (often referred to as "antisymmetric dependence of the dipole moment on the spins").¹⁻³¹ The other^{13,27,30-34} derives from ordering that may or may not involve canted spins, i.e., any canting is incidental ("symmetric dependence"). For clarity of presentation, the present paper deals exclusively with the case in which canting is essential. This case embodies the meaning of our term "canted-spin-caused electric dipoles."

One microscopic approach to this effect, due to Katsura, Nagaosa, and Balatzky (KNB),⁴ is derived by considering a model containing a pair of magnetic ions whose average spins $\mathbf{S}_a, \mathbf{S}_b$ are constrained to be in arbitrary directions. Such a constraint is imagined to result from exchange and anisotropy fields originating from the long-range-ordered magnetic state of the crystal. For example, the magnetic state might be a spiral, and the ion pair considered would be any neighboring pair participating in the spiral (with canted spins). In Ref. 4, it is found that the electron density becomes distorted by a combination of spin-orbit coupling V_{SO} and interionic electron hopping t . To leading order in t and V_{SO} , an electric dipole moment is found, given by

$$c\mathbf{R} \times (\mathbf{S}_a \times \mathbf{S}_b), \quad (1)$$

where \mathbf{R} is the displacement of one ion relative to the other, and c is a coefficient, discussed below.

Sergienko and Dagotto⁹ also considered a pair of magnetic atoms with canted spins, and noted that the Dzyaloshinskii-Moriya (DM) term, $\mathbf{D} \cdot \mathbf{S}_a \times \mathbf{S}_b$, in the superexchange energy also gave the same form when the intervening oxygen ion was

allowed to move off center. This is referred to as spin-lattice interaction, or magnetostriction.

A different approach is based on the complete crystal with spiral-like spin ordering; it has led to results consistent with (1). A derivation in this vein based on spin-lattice interactions by Harris *et al.*¹⁰ has been given; they consider magnetostriction both of the type coming from the DM coupling, which originates in the antisymmetric part of the exchange tensor, and that coming from the symmetric part; see also Ref. 31. There are also phenomenological derivations of magneto-ferroelectricity using symmetry arguments via Landau theory^{3,16,24,33} and Landau-Ginzburg theory.⁸

Also relevant here is a model [11] that is closely related to the KNB approach, again involving a pair of atoms, small hopping, and spin-orbit coupling. In Ref. 11(a), the expression (1) was found, where the assumption was made that the spatial symmetry of the situation was the symmetry of a pair of points in space, an assumption also made in Refs. 4 and 9. However, in Ref. 11(b), a lower symmetry was studied, which led to the possibility of another component of the dipole, namely in the direction

$$\mathbf{S}_a \times \mathbf{S}_b, \quad (2)$$

thus questioning the generality of (1). [The lower symmetry caused by orbital ordering was considered in Ref. 13, yet no additional terms like (2) were found. An explanation of this apparent dilemma can be found in Sec. II, Case 1, example (c).] This question was also raised, considering extended systems, in Refs. 12 and 21. In Ref. 12, experimental evidence in CuFeO_2 (Ref. 20) for this new possibility, occurring in the proper screw structure, was noted; a symmetry argument based on the observed spiral was given (Ref. 12), as well as a suggested microscopic mechanism behind the observation (to be discussed further below). A similar situation was found in CuCrO_2 .²⁸ In connection with Ref. 21, the question was answered in Ref. 16, where it was shown by an experimental

example, $\text{RbFe}(\text{MoO}_4)_2$ (RFMO), and a Landau theory analysis, that this $\mathbf{S}_a \times \mathbf{S}_b$ component can exist.

In overlapping time frames, a paper by Jia *et al.*¹³ followed the basic approach of Katsura *et al.*, considering a system with two magnetic atoms. In addition to giving a serious estimate of the coefficient c in (1), more general considerations added to (1) two additional terms. One is the well-known exchange striction (which does not concern us here because it does not require spin-canting), while the other is a new type of term, proportional to

$$(\mathbf{R} \cdot \mathbf{S}_a)\mathbf{S}_a - (\mathbf{R} \cdot \mathbf{S}_b)\mathbf{S}_b, \quad (3)$$

where $\mathbf{S}_a, \mathbf{S}_b$ are unit vectors. It is seen that this gives nonzero \mathbf{p} only if the spins are not collinear, which conforms to our general idea, in fact the precise definition, of a ‘‘canted-spin-caused’’ electric dipole. One notices that unlike the previous forms, which are bilinear in the two spins, this falls under the general heading of being quadratic in the spins. Arima¹² refers to this result, and generalizes it in a way that leads to a polarization parallel to the spiral wave vector \mathbf{Q} in a ‘‘proper screw structure’’ (a spiral where the spin plane is normal to \mathbf{Q}). [Since $\mathbf{Q} \parallel \mathbf{R}$ in his case, (3) clearly would give zero for such a spiral.] We will point out (in Sec. IV) a different microscopic mechanism that also gives \mathbf{p} in the direction of $\mathbf{S}_a \times \mathbf{S}_b$, which may be responsible for the behavior observed in the proper screw structure, and that also applies to RFMO (which is not a proper screw structure). (This mechanism is linear in the spin-orbit coupling strength while Arima’s is quadratic.)

Thus we see a veritable zoo of forms for the canted-spin caused dipole moment. One must ask, what others might exist? A common theme in all those mentioned is that they are quadratic in the pair of spins. The theory presented here considers the most general quadratic function that represents canted-spin-caused dipoles, and analyzes various forms allowed under whatever symmetry is ‘‘seen’’ by the pair of magnetic ions.³⁵ Since it includes the cases already known, it represents a general unified picture of the possible forms. The theory is model-independent and local (treating a single pair of magnetic ions or atoms). It is closely analogous to an argument leading to the conditions on the DM vector \mathbf{D} (Moriya’s rules) imposed by the symmetries of the magnetically disordered crystal.³⁶

The results show that forms far more general than (1), (2), and (3) are to be expected in general, and which symmetries, or, rather, their absence, are required for the more general forms. The theory also offers an explanation for the fact that (1) is found in many materials whereas the other forms have been found in relatively few (as far as we are aware). The analysis leads to the suggestion of new terms omitted from the microscopic theories. And it predicts an unusual antiferroelectric ordering in the antiferromagnetically and ferroelectrically ordered phase of $\text{RbFe}(\text{MoO}_4)_2$.

To apply this local theory to solids, one must determine how \mathbf{p} for a single bond propagates through the crystal. This is discussed through a few examples.

Section II reviews an analysis of the scalar quantity $\mathbf{D} \cdot (\mathbf{S}_a \times \mathbf{S}_b)$ that derives symmetry restrictions on the DM vector \mathbf{D} (Moriya’s rules), and applies an analogous analysis to the dipole moment \mathbf{p} , which is of course a vector. Essential to

the latter is expressing \mathbf{p} as a general homogeneous quadratic function of \mathbf{S}_a and \mathbf{S}_b . This restriction is made in the spirit of leading-order perturbation theory treating the hopping, spin-orbit coupling, and/or magnetostrictive atomic displacements as small. It applies to the approaches of KNB and related, as well as to the spin-lattice interaction approach of Ref. 9 and the corresponding work of Harris *et al.*,¹⁰ and to the problem of CuXO_2 , where $X = \text{Fe}, \text{Cr}$.^{12,20,28} Section III presents examples in crystals, some ideal, and some corresponding to the structures of real multiferroic crystals. Section IV contains some concluding remarks. Appendix A discusses the general bilinear function of two spins, with matrix B of the quadratic form for each component of \mathbf{p} . It shows that the most general spin-canted-caused dipole form originates from the antisymmetric part of B , and is linear in $\mathbf{S}_a \times \mathbf{S}_b$. We also consider, in the text, the most general *quadratic* function of the spins, and find additional contributions to \mathbf{p} , a special case of which is of form (3). Thus the overall results generalize all known forms. Appendix B describes the simple microscopic model¹¹ and its application as a check on the results of the abstract model-independent symmetry arguments.

II. SYMMETRY ANALYSIS OF THE ELECTRIC DIPOLE PRODUCED BY TWO CANTED SPINS

We begin by reviewing an argument leading to Moriya’s rules. (Moriya³⁶ states ‘‘the rules are obtained easily’’; he also gives an explicit formula for \mathbf{D} . It is not clear if he obtained the rules through his formula or some other way.) One considers the possible existence of a term in the energy of the form $E_{\text{DM}} = \mathbf{D} \cdot (\mathbf{S}_a \times \mathbf{S}_b)$, where \mathbf{S}_a and \mathbf{S}_b are the spins at sites A and B , respectively. \mathbf{D} is ‘‘a constant vector,’’ to quote Moriya.³⁶ Its sign obviously depends on the (arbitrary) order chosen to write the spins in the cross-product. If one adheres to a choice, e.g., spin at position $A \times$ spin at position B , then \mathbf{D} is a constant. That is, it is a property of the structure, atom-pair plus surroundings, exclusive of magnetic ordering and spin-orbit coupling. One explores the conditions imposed on \mathbf{D} by possible symmetries of the structure (without spin ordering), i.e., rotations that return the two sites plus surroundings to itself, with the requirement that E_{DM} be unchanged (as a term in a Hamiltonian, it is a scalar under such operations). It is important that \mathbf{D} is fixed in the structure (as seen in Moriya’s mathematical expression for it), so that \mathbf{D} is the same before and after the operation, emphasizing again that the order of the spins remains, spin at $A \times$ spin at B .

As a first illustration, inversion about the coordinate origin O in Fig. 1 simply interchanges \mathbf{S}_a and \mathbf{S}_b , so that for the new spin at site A , $\mathbf{S}'_a = \mathbf{S}_b$ and $\mathbf{S}'_b = \mathbf{S}_a$. Assuming inversion is a symmetry of the structure, one concludes $\mathbf{D} \cdot \mathbf{S}_a \times \mathbf{S}_b = \mathbf{D} \cdot \mathbf{S}'_a \times \mathbf{S}'_b = -\mathbf{D} \cdot \mathbf{S}_b \times \mathbf{S}_a$ for arbitrary $\mathbf{S}_a, \mathbf{S}_b$. Moriya’s Rule 1 follows: Given this inversion symmetry, $\mathbf{D} = \mathbf{0}$. Next consider Rule 2. Suppose a mirror plane perpendicular to AB passes through O . Then the transformed spins are

$$\begin{aligned} \mathbf{S}'_a &= \hat{\mathbf{x}}S_{bx} - \hat{\mathbf{y}}S_{by} - \hat{\mathbf{z}}S_{bz}, \\ \mathbf{S}'_b &= \hat{\mathbf{x}}S_{ax} - \hat{\mathbf{y}}S_{ay} - \hat{\mathbf{z}}S_{az}, \end{aligned} \quad (4)$$

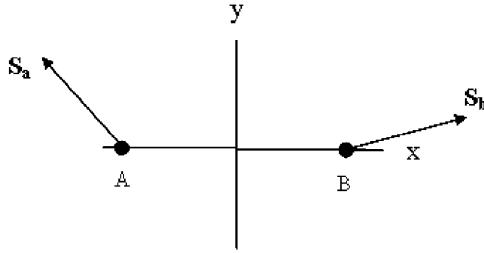


FIG. 1. The coordinate system and an example of the two spins. The z direction out of the paper.

which yields

$$\mathbf{S}'_a \times \mathbf{S}'_b = -\hat{x}(\mathbf{S}_a \times \mathbf{S}_b)_x + \hat{y}(\mathbf{S}_a \times \mathbf{S}_b)_y + \hat{z}(\mathbf{S}_a \times \mathbf{S}_b)_z. \quad (5)$$

Again, equating $\mathbf{D} \cdot \mathbf{S}_a \times \mathbf{S}_b = \mathbf{D} \cdot \mathbf{S}'_a \times \mathbf{S}'_b$ gives $D_x = 0$ (Rule 2). This procedure can be seen to yield all five rules. (We have used the axial-vector property of the spins; the results are unchanged if they are considered vectors.)

Now consider the electric dipole moment \mathbf{p} , a vector. (We find it convenient to use a different notation from that in the abstract.) As motivated above, we consider \mathbf{p} caused by a pair of spins as the general quadratic function,

$$\mathbf{p} = \sum_{\gamma, i, j, \nu, \mu} \hat{\gamma} B_{\gamma i j \nu \mu} S_{i \nu} S_{j \mu}, \quad (6)$$

where γ , ν , and μ run over the Cartesian coordinates, x, y, z , $\hat{\nu}$ being the corresponding unit vectors with $\hat{\nu} \cdot \hat{\mu} = \delta_{\nu \mu}$, and i, j run over the site or spin labels, a, b . We consider separately the two cases, $i \neq j$ and $i = j$.

Case 1: $i \neq j$. Equation (6) becomes

$$\mathbf{p} = \sum_{\gamma, \nu, \mu} \hat{\gamma} B_{\gamma \nu \mu} S_{a \nu} S_{b \mu}, \quad (7)$$

where $B_{\gamma \nu \mu} = B_{\gamma a b \nu \mu} + B_{\gamma b a \nu \mu}$. In Appendix A it is shown that for this function (which is bilinear in the spins) to represent a canted-spin-caused dipole, it must be a function of $\mathbf{S}_a \times \mathbf{S}_b \equiv \mathbf{W}$ that is linear homogeneous in \mathbf{W} , its most general form being

$$\mathbf{p} = \sum C_{\nu \mu} \hat{\nu} \hat{\mu} \cdot \mathbf{W} \equiv \vec{\mathcal{C}} \cdot \mathbf{W}. \quad (8)$$

Here $C_{\nu x} = B_{\nu y z}^a$, $C_{\nu y} = B_{\nu z x}^a$, $C_{\nu z} = B_{\nu x y}^a$, with $B_{\gamma \nu \mu}^a = (B_{\gamma \nu \mu} - B_{\gamma \mu \nu})/2$. The form (8) also applies to the spin-lattice mechanism via the DM term ($\vec{\mathcal{C}}$ is related to the derivatives of the DM vector \mathbf{D} with respect to lattice distortions from the nonmagnetic crystal structure).

The symmetric contribution, from $B_{\gamma \nu \mu}^s = (B_{\gamma \nu \mu} + B_{\gamma \mu \nu})/2$, is also important to multiferroics in general. But for simplicity, we focus in this paper on the canted-spin-caused part.

To connect with existing literature, we write $C_{\nu \mu} = S_{\nu \mu} + \mathcal{A}_{\nu \mu}$, where S and \mathcal{A} are the symmetric and antisymmetric parts of the matrix \mathcal{C} , allowing the separation of \mathbf{p} into the corresponding terms: $\mathbf{p} = \mathbf{p}_S + \mathbf{p}_A$. (There is a very different sense in which \mathbf{p} is written as a sum $\mathbf{p}_S + \mathbf{p}_A$. Namely, in Ref. 31 and elsewhere, \mathbf{p}_S is attributed to that obtained from the spin-lattice interaction associated with the symmetric part

of the exchange tensor, \mathbf{p}_A , to the antisymmetric part. In the present work, for the model of spin-lattice interaction, both \mathbf{p}_S and \mathbf{p}_A originate from the antisymmetric part of the exchange tensor.) In particular, from (8) it follows that

$$\mathbf{p}_A = \hat{x}(\mathcal{A}_{xy} W_y + \mathcal{A}_{xz} W_z) + \hat{y}(\mathcal{A}_{yx} W_x + \mathcal{A}_{yz} W_z) + \hat{z}(\mathcal{A}_{zx} W_x + \mathcal{A}_{zy} W_y). \quad (9)$$

It is easily verified that this is

$$\mathbf{p}_A = \mathbf{d} \times \mathbf{W}, \quad (10)$$

$$\mathbf{d} = -(\hat{x}\mathcal{A}_{yz} + \hat{y}\mathcal{A}_{zx} + \hat{z}\mathcal{A}_{xy}).$$

Thus we have connected to the important term (1), which is a special case of (10) in which $\mathbf{d} = \mathbf{d}_{\parallel}$, along \mathbf{R} , or \hat{x} in the coordinate system of Fig. 1.

Recall that standard transformation theory in which we apply a rotation $\vec{U} \equiv \sum U_{\nu \mu} \hat{\nu} \hat{\mu}$ to (8) gives

$$\mathbf{p}' \equiv \vec{U} \cdot \mathbf{p} = \vec{\mathcal{C}}' \cdot \mathbf{W}',$$

where $\vec{\mathcal{C}}' = \sum C'_{\nu \mu} \hat{\nu} \hat{\mu}$, $C' = U C U^{-1}$, and $\mathbf{W}' = \vec{U} \cdot \mathbf{W} (= \mathbf{S}'_a \times \mathbf{S}'_b)$. We consider U as real and unitary. When U is a symmetry operation, as described above, the matrix \mathcal{C} is unchanged, i.e., $C' = \mathcal{C}$. Thus our fundamental equation for applying symmetry operations is

$$\mathbf{p}' = \sum C_{\nu \mu} \hat{\nu} \hat{\mu} \cdot \mathbf{W}'. \quad (11)$$

The relation $C' = \mathcal{C}$ is analogous to \mathbf{D} being unchanged under a symmetry operation.³⁶

We now apply rotations that leave the structure, sites A and B plus the magnetically disordered environment, unchanged, and require \mathbf{p} to satisfy its vector property. This requirement is applied for each of Moriya's list of (five) rotations (all possibilities that take the sites A and B into themselves).

(i) *Inversion through O .* As before, $\mathbf{W}' = -\mathbf{W}$. Thus (11) gives $\mathbf{p}' = -\mathbf{p}$. This is precisely what a vector should do under inversion. Thus *inversion invariance gives no restriction on \mathbf{p} .*

(ii) *Mirror $\perp AB$.* The reflected \mathbf{W} is given in (5): $(W'_x, W'_y, W'_z) = (-W_x, W_y, W_z)$. Thus (11) becomes

$$\begin{aligned} \mathbf{p}' = & (-C_{xx} W_x + C_{xy} W_y + C_{xz} W_z, \\ & -C_{yx} W_x + C_{yy} W_y + C_{yz} W_z, \\ & -C_{zx} W_x + C_{zy} W_y + C_{zz} W_z). \end{aligned}$$

The vector property says $\mathbf{p}' = (-p_x, p_y, p_z)$, with p_ν from (8). Therefore, \mathcal{C} must have the form

$$\mathcal{C} = \begin{pmatrix} C_{xx} & 0 & 0 \\ 0 & C_{yy} & C_{yz} \\ 0 & C_{zy} & C_{zz} \end{pmatrix}. \quad (12)$$

We see that this symmetry requires the only contribution to $\mathcal{A}_{\nu \mu}$ be \mathcal{A}_{yz} . Thus (10) gives $\mathbf{d} = -\hat{x}\mathcal{A}_{yz}$, i.e., \mathbf{d}_{\parallel} , parallel (or antiparallel) to \mathbf{R} .

(iii) *Mirror includes AB .* We can take the mirror as the xy plane. Since this involves no interchange of \mathbf{S}_a and \mathbf{S}_b , \mathbf{W}

behaves as a pseudovector so $\mathbf{W}' = (-W_x, -W_y, W_z)$. Then (11) reads

$$\begin{aligned} \mathbf{p}' = & (-C_{xx}W_x - C_{xy}W_y + C_{xz}W_z, \\ & -C_{yx}W_x - C_{yy}W_y + C_{yz}W_z, \\ & -C_{zx}W_x - C_{zy}W_y + C_{zz}W_z). \end{aligned}$$

Comparing with the vector property $\mathbf{p}' = (p_x, p_y, -p_z)$ leads to the restricted form

$$\mathcal{C} = \begin{pmatrix} 0 & 0 & C_{xz} \\ 0 & 0 & C_{yz} \\ C_{zx} & C_{zy} & 0 \end{pmatrix}. \quad (13)$$

This result implies \mathbf{d} lies in the mirror plane.

(iv) *Twofold rotation axis* $\perp AB$. We can take this as the z axis, so that $\mathbf{S}'_a = (-S_{bx}, -S_{by}, S_{bz})$ and $a \leftrightarrow b$. This gives

$$\mathbf{W}' = (W_x, W_y, -W_z).$$

Thus (11) becomes

$$\begin{aligned} \mathbf{p}' = & (C_{xx}W_x + C_{xy}W_y - C_{xz}W_z, \\ & C_{yx}W_x + C_{yy}W_y - C_{yz}W_z, \\ & C_{zx}W_x + C_{zy}W_y - C_{zz}W_z). \end{aligned}$$

Comparing with the vector property $\mathbf{p}' = (-p_x, -p_y, p_z)$ yields the same \mathcal{C} as (13). So this symmetry implies $\mathbf{d} \perp$ rotation axis.

(v) *n-fold axis along AB*, $n \geq 2$. Here $\mathbf{W}' = (W_x, cW_y - sW_z, sW_y + cW_z)$, where $(c, s) \equiv (\cos \theta, \sin \theta)$, θ = the rotation angle. The vector property of \mathbf{p} demands $\mathbf{p}' = (p_x, cp_y - sp_z, sp_y + cp_z)$. We again equate this expressed in terms of \mathbf{W} [using (8)] with the corresponding equation for \mathbf{p}' given by (11). For $n > 2$, this leads to

$$\mathcal{C} = \begin{pmatrix} C_{xx} & 0 & 0 \\ 0 & C_{yy} & C_{yz} \\ 0 & -C_{yz} & C_{yy} \end{pmatrix} \quad \text{for } n > 2. \quad (14)$$

While this result is valid for all $n > 2$, it changes for $n = 2$, as follows: The conditions $C_{zz} = C_{yy}$ and $C_{zy} = -C_{yz}$ no longer hold. The reason for the difference between $n = 2$ and $n \neq 2$ is that for $n = 2$ ($\theta = \pi$) there is no mixing between y and z components, unlike the case $n \neq 2$. In either case, the form of \mathcal{C} implies $\mathbf{d} = \mathbf{d}_{\parallel}$. In contrast to the dipole moment \mathbf{p} , it is interesting to note that the consequences of these symmetry operations on the DM vector \mathbf{D} are independent of n .³⁶

These results were checked against the microscopic model calculation in Ref. 11 (see Appendix B).

An important conclusion to be drawn from these results is that the contribution to \mathbf{p} coming from $\mathbf{d}_{\parallel} \times (\mathbf{S}_a \times \mathbf{S}_b) \equiv \mathbf{p}_{A,1}$ [the form (1)] is allowed in every one of the symmetry operations. It is robust; no symmetry can deny its existence as a contribution to the electric dipole moment. The other part of \mathbf{p}_A , namely $\mathbf{d}_{\perp} \times (\mathbf{S}_a \times \mathbf{S}_b) \equiv \mathbf{p}_{A,2}$, plus the contributions from the symmetric part, \mathcal{S} , of \mathcal{C} , have restrictions imposed by crystal symmetries that may exist.

The other special contribution, $\mathbf{p} \propto \mathbf{S}_a \times \mathbf{S}_b = \mathbf{W}$, discussed in the Introduction, is seen to be nonexistent if symmetries 3. or 4. exist. In general, contributions from $\sum \hat{v} C_{vv} W_v$ “contain” \mathbf{W} , but are not in its direction. Exceptions occur

when \mathbf{W} is in the x direction (along AB), and the symmetries present are 2., and/or 5., in which case $\mathbf{p} \propto \mathbf{W}$.

A few examples will illustrate the physical meaning of these single-bond results.

(a) Suppose the only symmetry is 2., mirror $\perp AB$, in which (12) holds. In this case, we see that $\mathbf{d} = \mathbf{d}_{\parallel}$. Consider \mathbf{W} in turn along the x, y, z directions. $\mathbf{W} = \hat{x} : \mathbf{p} = \hat{x} C_{xx}$; $\mathbf{W} = \hat{y} : \mathbf{p} = \hat{y} C_{yy} + \hat{z} C_{zy}$; $\mathbf{W} = \hat{z} : \mathbf{p} = \hat{y} C_{yz} + \hat{z} C_{zz}$. When $\mathbf{W} = \hat{y}$ or \hat{z} , the contribution from $\mathbf{d} \times \mathbf{W}$ is the z component C_{zy} or the y component C_{yz} . That there is no requirement that $\mathbf{d} = \mathbf{0}$, i.e., $C_{yz} = C_{zy}$, makes sense, since symmetry 2. allows the xy and xz planes to be nonequivalent.

(b) An example showing the new term \mathbf{d}_{\perp} : Suppose that the only symmetry is Mirror, includes AB (3.). Assume $\mathbf{W} = \hat{z}$. Then one can read off from (13) that $\mathbf{p} = \hat{y} C_{yz} + \hat{x} C_{xz}$. The respective terms are $\propto \mathbf{d}_{\parallel} \times \mathbf{W}$ and $\mathbf{d}_{\perp} \times \mathbf{W}$.

(c) An example relevant to the present literature is the following dilemma (mentioned earlier): In the case of orbital ordering considered by Jia *et al.*,¹³ the bond symmetry is rather low; so why does their calculation not yield one of the new forms, e.g., $\mathbf{p} \propto \mathbf{S}_a \times \mathbf{S}_b$? The answer is given nicely by our results: The d orbitals at sites A and B are the e_g states $3x^2 - r^2$ and $3y^2 - r^2$, respectively. Such a charge configuration has the bond symmetries, reflection in plane containing AB (3.), and AB is a twofold axis (5.), and only these. Looking at the corresponding \mathcal{C} matrices (13) and the appropriately modified (14) for $n = 2$, one sees that the only possibility is $\mathbf{p} = \mathbf{d}_{\parallel} \times \mathbf{W}$. That is, the *particular* lowering of the bond symmetry caused by orbital ordering is not sufficient to modify the form (1) for the dipole moment.

Case 2: $i = j$. Equation (6) now becomes

$$\mathbf{p} = \sum_{\gamma, \nu, \mu} \hat{\gamma} B_{\gamma \nu \mu} S_{\nu \mu} + \sum_{\gamma, \nu, \mu} \hat{\gamma} B_{\gamma \nu \mu} S_{\nu \mu}. \quad (15)$$

Only the symmetric part, $B_{\gamma i \nu \mu} + B_{\gamma i \mu \nu}$ of $B_{\gamma i \nu \mu}$, for $i = a$ or b , contributes. In order that this represent a canted-spin-caused dipole, i.e., that it is zero for collinear spins of arbitrary direction, one sees that

$$B_{\gamma a \nu \mu} + B_{\gamma b \nu \mu} = 0.$$

That is, the part of (15) that gives a canted-spin-caused electric dipole is of the form

$$\begin{aligned} \mathbf{p}_0 &= \sum \hat{\gamma} B_{\gamma \nu \mu} (S_{\nu \mu} - S_{\mu \nu}) \\ &\equiv \sum \hat{\gamma} B_{\gamma \nu \mu} \Gamma_{\nu \mu}, \end{aligned} \quad (16)$$

where $B_{\gamma \nu \mu} = B_{\gamma \mu \nu}$. Clearly $\Gamma_{\nu \mu} = \Gamma_{\mu \nu}$. It will be seen that this contains the form (3) as a special case.

We now apply the symmetry procedure to (16).

(i) *Inversion through O*. Again, $\mathbf{S}'_a = \mathbf{S}_b, \mathbf{S}'_b = \mathbf{S}_a$. Thus the right-hand side of (16) changes sign, so inversion invariance places no restriction on $B_{\gamma \nu \mu}$.

(ii) *Mirror* $\perp AB$. From (4) one readily sees that

$$\Gamma'_{\nu \nu} = -\Gamma_{\nu \nu}, \Gamma'_{xy} = \Gamma_{xy}, \Gamma'_{xz} = \Gamma_{xz}, \Gamma'_{yz} = -\Gamma_{yz}.$$

Using these relations and demanding the vector property $\mathbf{p}'_0 = (-p_x, p_y, p_z)$ yields

$$\begin{pmatrix} B_{xxx} & 0 & 0 \\ 0 & B_{xyy} & B_{xyz} \\ 0 & B_{xyy} & B_{xzz} \end{pmatrix}, \begin{pmatrix} 0 & B_{yxy} & B_{yxz} \\ B_{yxy} & 0 & 0 \\ B_{yxz} & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & B_{zxy} & B_{zxx} \\ B_{zxy} & 0 & 0 \\ B_{zxx} & 0 & 0 \end{pmatrix}, \quad (17)$$

where the three matrices represent $B_{\gamma\nu\mu}$ for $\gamma = x, y, z$, respectively, reading from left to right.

(iii) *Mirror includes AB*. Taking the mirror as the xy plane, we have

$$\Gamma'_{\nu\nu} = \Gamma_{\nu\nu}, \quad \Gamma'_{xy} = \Gamma_{xy}, \quad \Gamma'_{xz} = -\Gamma_{xz}, \quad \Gamma'_{yz} = -\Gamma_{yz}.$$

This plus invoking the vector property of \mathbf{p} yields

$$\begin{pmatrix} B_{xxx} & B_{xxy} & 0 \\ B_{xxy} & B_{xyy} & 0 \\ 0 & 0 & B_{xzz} \end{pmatrix}, \begin{pmatrix} B_{yxx} & B_{yxy} & 0 \\ B_{yxy} & B_{yyy} & 0 \\ 0 & 0 & B_{yzz} \end{pmatrix}, \begin{pmatrix} 0 & 0 & B_{zxx} \\ 0 & 0 & B_{zyz} \\ B_{zxx} & B_{zyz} & 0 \end{pmatrix}. \quad (18)$$

(iv) *Twofold rotation \perp AB*. Taking the rotation axis as the z axis gives

$$\Gamma'_{\nu\nu} = -\Gamma_{\nu\nu}, \quad \Gamma'_{xy} = -\Gamma_{xy}, \quad \Gamma'_{xz} = \Gamma_{xz}, \quad \Gamma'_{yz} = \Gamma_{yz},$$

which yields the identical form for the $B_{\gamma\nu\mu}$ matrices as (18).

(v) *n -fold axis along AB, $n \geq 2$* . We again find that the form forced by rotation invariance depends on n . We discuss two examples, $n = 2$ and 4. In general, $\Gamma'_{xx} = \Gamma_{xx}$ of course.

Beginning with $n = 2$, we have

$$\Gamma'_{\nu\nu} = \Gamma_{\nu\nu}, \quad \Gamma'_{xy} = -\Gamma_{xy}, \quad \Gamma'_{xz} = -\Gamma_{xz}, \quad \Gamma'_{yz} = \Gamma_{yz}. \quad (19)$$

The form of the resulting $B_{\gamma\nu\mu}$ matrices is identical to (17).

For $n = 4$, one readily finds that

$$\Gamma'_{yy} = \Gamma_{zz}, \quad \Gamma'_{zz} = \Gamma_{yy}, \quad \Gamma'_{xy} = -\Gamma_{xz}, \quad \Gamma'_{xz} = \Gamma_{xy}, \quad \Gamma'_{yz} = -\Gamma_{yz}, \quad (20)$$

which lead to

$$\begin{pmatrix} B_{xxx} & 0 & 0 \\ 0 & B_{xyy} & 0 \\ 0 & 0 & B_{xyy} \end{pmatrix}, \begin{pmatrix} 0 & B_{yxy} & B_{yxz} \\ B_{yxy} & 0 & 0 \\ B_{yxz} & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -B_{yxz} & B_{yxy} \\ -B_{yxz} & 0 & 0 \\ B_{yxy} & 0 & 0 \end{pmatrix}. \quad (21)$$

Comparison of the x matrix with that in (17), which holds for $n = 2$, shows that going from $n = 2$ to the higher symmetry $n = 4$ gives the reduction $B_{xyy} - B_{xzz} \rightarrow 0$ and $B_{xyz} \rightarrow 0$. For the y and z matrices, the higher symmetry introduces no new zeros but brings in a relation between these matrices.

Finally, to compare with (3), we consider the case in which all five symmetries hold, taking the case of fourfold rotation in symmetry 5. We find the form of the B tensor is

$$\begin{pmatrix} B & 0 & 0 \\ 0 & C & 0 \\ 0 & 0 & C \end{pmatrix}, \begin{pmatrix} 0 & D & 0 \\ D & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & D \\ 0 & 0 & 0 \\ D & 0 & 0 \end{pmatrix}. \quad (22)$$

(Here $B = B_{xxx}$, $C = B_{xyy}$, and $D = B_{yxy}$.) This gives

$$\mathbf{p} = \hat{x}(B - C)(S_{ax}^2 - S_{bx}^2) + 2D[\hat{y}(S_{ax}S_{ay} - S_{bx}S_{by}) + \hat{z}(S_{ax}S_{az} - S_{bx}S_{bz})]. \quad (23)$$

The corresponding term in Ref. 13 [(3) in the present paper] is

$$\mathbf{p} \propto \hat{x}(S_{ax}^2 - S_{bx}^2) + \hat{y}(S_{ax}S_{ay} - S_{bx}S_{by})\hat{z}(S_{ax}S_{az} - S_{bx}S_{bz}). \quad (24)$$

Thus it is seen that (3) is the special case of our result (23) where $B - C = 2D$.

A particular case studied in Ref. 13 applies to Mn^{3+} as in the manganites, e.g., TbMnO_3 , where the t_{2g} states are filled and the e_g states are orbitally ordered (the spins on each ion are parallel). Jia *et al.* find no contribution of the form (3) whenever the t_{2g} states with parallel spins are filled.¹³ This fact motivates the application of our theory to this example. The e_g orbitals on the two sites are as described in example (c) under Case 1. The corresponding symmetry is twofold axis along AB and two mirror planes, xy and xz . Applying our results to these cases, we find

$$\mathbf{p} = \hat{x} \sum_{\nu=x,y,z} a_\nu (S_{a\nu}^2 - S_{b\nu}^2) + \sum_{\nu=y,z} 2\hat{\nu} d_\nu (S_{ax}S_{a\nu} - S_{bx}S_{b\nu}), \quad (25)$$

where the a_ν and d_ν comprise five arbitrary coefficients.

Thus the symmetry does not require the vanishing of this type of contribution to \mathbf{p} . This lack of generality within the symmetry of the model¹³ indicates that other terms should enter. We suggest that one candidate for such terms is the modification of the spin-orbit coupling used in Ref. 13 due to the presence of the O^{2-} charge near each Mn and the Mn^{3+} charges near the oxygen ion. Such effects would not modify the symmetry of the superexchange model of Ref. 13. (See also the related discussion in Sec. IV.)

III. SOME APPLICATIONS TO CRYSTALS (PROPAGATION OF SINGLE-BOND RESULTS)

Application of these local or bond results requires their propagation to all other equivalent bonds. In this sense, this approach becomes “global,” as is the powerful Landau theory of continuous phase transitions, also based in an essential way on symmetry considerations. The approaches are, nevertheless, different. One aspect of the difference is that the present theory applies to any phase of the crystal, whether or not it was reached through a continuous phase transition from a known phase, unlike the Landau theory. Another symmetry approach, exemplified by the analyses in Refs. 12 and 29 considers the symmetry of the magnetically ordered crystal, and sees if that symmetry is consistent with having a

macroscopic electric polarization. In common with the present approach, its validity is independent of how the phase was reached; it differs, e.g., in that it only considers the ferroelectric response, whereas the present local symmetry approach allows prediction of various complex antiferroelectric structures.

Case (i): $i \neq j$. The simplest application is a linear chain, which spins in a line with no other objects around, as a check on previously known results, given that the spins form a simple spiral. Here the C matrix is the same for every nearest-neighbor (NN) bond. In the usual case, the plane of the spins includes the chain direction, which is of course the direction of the spiral wave vector. This sort of spiral, often called, appropriately, a cycloid, is actually used to understand many real materials.^{3,4,7,12,14,25–27,37,38} But we can leave the direction of the spin plane (normal to \mathbf{W}) arbitrary for the present discussion. In this case of high bond symmetry, every one of Moriya's symmetries applies. Equations (13) and (14) imply

$$C = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & C_{yz} \\ 0 & -C_{yz} & 0 \end{pmatrix}. \quad (26)$$

Hence C is antisymmetric, $\mathbf{d} = \mathbf{d}_{\parallel}$, so that $\mathbf{p} = \mathbf{d}_{\parallel} \times \mathbf{W}$. When \mathbf{W} is in the z direction (spins lie in the x - y plane), this gives the expected result, \mathbf{p} in the y direction. This is easily generalized to one-dimensional structures of lower symmetry by imagining the chain decorated with other charges; in general, each bond \mathbf{p} can, *a priori*, be in any direction. If each decorated bond is just translated, then the total \mathbf{p} will have other components. For example, if symmetries 3. and 4. are violated and 5. remains, then \vec{C} is given by (14) for $n > 2$; in particular, if in addition \mathbf{W} is in the x direction, then it follows that total \mathbf{p} is in the direction of \mathbf{W} . The same conclusion holds for $n = 2$. This case is that of Arima,¹² a "proper screw" structure with \mathbf{p} in the direction of the spiral wave vector. It is also related to the following.

The second example we discuss is $\text{RbFe}(\text{MoO}_4)_2$ (RFMO), the ferroelectricity of which was studied extensively by Kenzelmann *et al.*¹⁶ While the observed ferroelectricity is well-understood by the Landau-theory analysis of Ref. 16, it is instructive to consider it from the point of view of the present, quite different, symmetry theory. We consider the low-temperature behavior.

The magnetism resides in triangular layers of Fe^{3+} ions whose spins lie in the planes, and form the well-known 120° spin order, which maintains the same handedness (the same \mathbf{W} for each NN bond) in translation from layer to layer. (One must remember that the arbitrary order taken in writing $\mathbf{W} = \mathbf{S}_a \times \mathbf{S}_b$ makes sense only in conjunction with the associated \vec{C} . One can make an assumption as to the order of the spins in \mathbf{W} , and thus the sign of \mathbf{p} , for one bond. Then all other bonds follow uniquely from crystal symmetry operations.) For the crystal structure, see Ref. 21, particularly Figs. 1(a) and 1(b), and Refs. 39 and 40, particularly Fig. 1 of Ref. 39; the low-temperature (nonmagnetic) space group is $P\bar{3}$. Other nonmagnetic ions between these layers cause the symmetries 3. and 4. to be violated. Whether or not any of the remaining symmetries exist, it is seen that a local electric dipole moment $\propto \mathbf{W}$, which lies \perp these planes, is allowed. Each plane ν possesses a total dipole moment \mathbf{P}_ν , as follows from the threefold axis of $P\bar{3}$, which implies that \vec{C} for every

bond within a plane is rotated by this operation. Also, the 120° spin structure has the same property. Further, we need to know if all planes produce the same moment, or might the sign alternate. Now $P\bar{3}$ implies a center of inversion between the magnetic planes that connect bonds in different planes, carrying all the complex nonmagnetic structure along via the inversion. Essential is the relation between the C matrices describing the surroundings of each of the inversion-related bonds. We determine this as follows. We have $\mathbf{p} = \vec{C} \cdot \mathbf{W}$, so that $I\mathbf{p} = I\vec{C}I \cdot I\mathbf{W}$. But $I\mathbf{W} = -\mathbf{W}$, as noted above. Since $I\mathbf{p} = -\mathbf{p}$, it follows quite generally that

$$I\vec{C}I = \vec{C}; \quad (27)$$

i.e., C is invariant under inversion. \mathbf{W} being the same for every plane, it follows that the planar \mathbf{P}_ν 's all have the same sign, resulting in a net nonzero polarization, as observed.

The authors note¹⁶ that the existence of a threefold axis \perp to the planes (the c axis) implies there cannot be a component of \mathbf{P} parallel to the planes. We can see this from our general expression, $\mathbf{p} = \hat{x}C_{xz} + \hat{y}C_{yz} + \hat{z}C_{zz}$, for our case, $\mathbf{W} \propto \hat{z}$: For each triangular plaquette, the x and y components will add to zero because of the threefold axis. On the other hand, these components $\perp \hat{z}$ will order *antiferroelectrically* in a 120° state because of the ordered spins and the threefold axis. If the high- T structure, space group $P\bar{3}m1$, held, then only the \mathbf{d}_{\parallel} term would survive, and that would imply that the projection of the bond dipole moments would each lie \perp to the bond. Figure 5 in an early effort (Ref. 35) shows this for a triangular plaquette. However, the true structure has the lower symmetry space group $P\bar{3}$; one can see (particularly with the help of Fig. 1 in Ref. 39) that none of Moriya's symmetry operations holds, so that any direction of \mathbf{p} for given spins in a bond is allowed by symmetry. We indicate this situation schematically for a single triangular plaquette in Fig. 2. The location of the electric moments at the midpoints of the triangle edges (the Kagomé structure, dual to the triangular lattice) is symbolic of the actual bond charge density found in the microscopic theories of Refs. 4, 13, and 11 [although, with the exception of Ref. 11, the high symmetry assumed in these calculations requires no component of $\mathbf{p} \parallel \mathbf{W}$]. Such a charge distribution

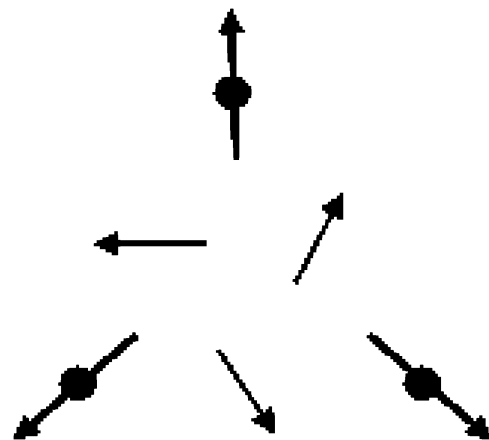


FIG. 2. Triangular plaquette of spins (darker arrows) and electric dipoles (lighter arrows) predicted for RFMO (schematic). The arrows represent the projections on the spin planes of the full dipoles.

would be ordered in the crystal (it is tied strongly to the magnetism), and would induce corresponding changes in ionic positions, which should help in its detection by diffraction methods.

Also the response of the multiferroic state to a uniform magnetic field \mathbf{H} might possibly give insight into this complex orientation structure of the local dipoles. The idea is, of course, that applying \mathbf{H} will distort the magnetic order, modifying \mathbf{W} and therefore the local dipoles \mathbf{p}_v . This idea was discussed in Ref. 41. In particular, applying \mathbf{H} in the plane of the spins in Fig. 2 would give a net dipole moment for the plaquette, considering the system of three spins as isolated. We have shown that for small $\mathbf{H} \parallel$ to one of the spins, the component of total polarization in an isolated triangular lattice with the 120° spin structure is of order H^2 . In RFMO there have appeared some limited experimental studies of the magnetic and electric (i.e., charge) properties in applied fields.¹⁶ These put \mathbf{H} parallel to the plane of the spins along a particular crystallographic direction, and presented information about the c -axis component of polarization, only as to whether it was zero or nonzero. The theory presented was for the zero-field case. In fact, the theory for $\mathbf{H} \neq \mathbf{0}$ is nonexistent as far as we are aware, and that is essentially because the particular magnetic structure in a field is complex and its origin has not been elucidated, particularly concerning the incommensurate component of the spiral wave vector along the c axis.⁴² See also Ref. 43. While such studies would be interesting, we will not consider them here.

Our last example concerns the materials CuFeO_2 and ACrO_2 ($A = \text{Cu, Ag}$), in which canted-spin-caused ferroelectricity was found.^{6,19,20,22,28} These materials have the magnetic ions (Fe^{3+} , Cr^{3+}) situated on triangular lattices (basal planes), and are of delafossite form. The canted spin states are spirals with wave vector $\mathbf{Q} = (q, q)$ in the plane and the spins lie in a plane such that $\mathbf{S}_a \times \mathbf{S}_b$ lies in the basal plane. The special case $\mathbf{S}_a \times \mathbf{S}_b \parallel \mathbf{Q}$ is known to occur in CuFeO_2 and CuCrO_2 .^{20,28} Importantly, in the latter cases the polarization lies parallel to \mathbf{Q} , i.e., in the direction $\mathbf{S}_a \times \mathbf{S}_b$, where the two spins are NN's along the \mathbf{Q} direction. As discussed above, there is a close relation between this structure and that of RFMO: the essential difference is that the magnetic anisotropy is easy plane for RFMO or easy axis for the former, as emphasized in Refs. 22 and 29. But in all these cases, the polarization is in the direction of $\mathbf{S}_a \times \mathbf{S}_b$. We just saw how our symmetry analysis gives results consistent with these facts for RFMO. Let us consider now the delafossites. Referring to Fig. 1 of Arima's paper,¹² one sees that the only one of the five symmetry operations that is satisfied for a NN Fe-Fe bond is a twofold rotation axis coinciding with AB (operation 5.), for which the C matrix is given by (14) appropriately modified for $n = 2$, where the bond is along the x direction. But $\mathbf{S}_a \times \mathbf{S}_b = \mathbf{W}$ is also in the x direction, giving $\mathbf{p} = C_{xx} \mathbf{W}$ (in the x direction), i.e., \mathbf{p} is in the direction of \mathbf{Q} as observed.

IV. CONCLUDING REMARKS

The robustness of $\mathbf{p}_{A,1} = \mathbf{R} \times (\mathbf{S}_a \times \mathbf{S}_b)$ under symmetry requirements may be why it has been found experimentally in many different materials, whereas only one of the many other possibilities given by the present theory has

been found, as far as we are aware, namely \mathbf{p} in the direction of $\mathbf{S}_a \times \mathbf{S}_b$, and only in three materials, namely CuFeO_2 ,²⁰ CuCrO_2 ,²⁸ and $\text{RbFe}(\text{MoO}_4)_2$ (RFMO).¹⁶

$\mathbf{p}_{A,2}$ shows new possibilities for the dipole moment produced by a pair of atoms with canted spins. For example, in the case that is familiar in many multiferroics, where $\mathbf{S}_a, \mathbf{S}_b$, and \mathbf{R} are coplanar, say in the x - y plane, then the already discovered possibility that \mathbf{p} has a y component (from $\mathbf{p}_{A,1}$) is now accompanied by the possibility of having a z component originating from $\mathbf{p}_{A,2}$. There can also be an x component ($\|\mathbf{S}_a \times \mathbf{S}_b\|$) originating from \mathbf{p}_S .

The results obtained here apply directly to model calculations based on clusters that contain a pair of magnetic atoms, as in Refs. 4, 13, and 9. The process of checking our symmetry results against the simple, idealized quantum-mechanical model¹¹ described in Appendix B goes further in that it suggests a microscopic mechanism for the case in which the dipole moment \mathbf{p} is in the direction of $\mathbf{S}_a \times \mathbf{S}_b$, which includes both the proper screw structure¹² and the spiral in RFMO.²¹ The mechanism, which should be valid in the approach of Refs. 4, 13, and 9, is the effect of the environment on the nature, or symmetry, of the spin-orbit interaction. The SO interaction in an isolated atom or ion is of the commonly used form $\propto \mathbf{l} \cdot \mathbf{s}$, and this is the form used in the theories of Refs. 4 and 13. However, this is just the special case of the more general form $\propto \nabla V(\mathbf{r}) \times \hat{\mathbf{p}} \cdot \mathbf{s}$ ($\hat{\mathbf{p}}$ is the momentum operator) that results when $V(\mathbf{r})$ is spherically symmetric, as assumed for the nucleus plus the other electrons on the atom. When the atom is in an environment of other charges outside the atom, $V(\mathbf{r})$ will have a nonspherically symmetric part.⁴⁴ This will reflect the symmetry of that environment and will lead to the other forms of the magnetically induced electric dipole. (This effect is implicit in the analysis of Ref. 9 via the microscopic theory behind the DM vector \mathbf{D} .³⁶) This mechanism differs substantially from Arima's:¹² this is linear in the SO coupling strength, whereas Arima's is second order. Of course, this contribution will generally be smaller than the intra-atomic (spherical) contribution, because the environmental charges are farther from the atom than the atomic charge, an effect ameliorated by the fact that the active electron states vanish at the nucleus, both for the magnetic ions and the oxygen. A crude estimate suggests that this mechanism is not negligible compared to the spherical term, originating in the d shell.

Our results of course suggest strongly that there will be materials that exhibit the new forms for \mathbf{p} . We have given three examples of the single form $\mathbf{p} \propto \mathbf{S}_a \times \mathbf{S}_b$, namely CuFeO_2 , CuCrO_2 , and RFMO. The observation of others would be of great interest in verifying the theory and deepening our understanding of these fascinating multiferroics.

We note that the present local or bond-symmetry approach can also be applied to the symmetric magnetostriction (the tensor $B_{\gamma\nu\mu}^s$ defined in Appendix A), which would include electric dipoles produced by collinear magnetic ordering.

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APPENDIX A: PROOF THAT EQ. (8) IS THE MOST GENERAL VECTOR FUNCTION OF SPINS $\mathbf{S}_a, \mathbf{S}_b$, BILINEAR IN THE SPINS, AND REPRESENTING “CANTED-SPIN-CAUSED” ELECTRIC DIPOLES

The most general vector function of spins bilinear in the spins $\mathbf{S}_a, \mathbf{S}_b$ is

$$\mathbf{p} = \sum_{\gamma, \nu, \mu} \hat{\gamma} B_{\gamma\nu\mu} S_{a\nu} S_{b\mu}, \quad (\text{A1})$$

where γ, ν, μ run over Cartesian components x, y, z . The spins are assumed to be of fixed length, so they can be taken as unit vectors (or, really, unit pseudovectors, but this is irrelevant here). The idea that \mathbf{p} be “caused” by spin canting is defined by the requirement $\mathbf{p} = \mathbf{0}$ if $\mathbf{S}_a = \pm \mathbf{S}_b$ for arbitrary \mathbf{S}_a . That is, \mathbf{p} vanishes whenever the spins are collinear (noncanted).

We can write

$$B_{\gamma\nu\mu} = B_{\gamma\nu\mu}^s + B_{\gamma\nu\mu}^a, \quad (\text{A2})$$

where $B_{\gamma\nu\mu}^s = B_{\gamma\mu\nu}^s, B_{\gamma\nu\mu}^a = -B_{\gamma\mu\nu}^a$, defining in the obvious correspondence \mathbf{p}_s and \mathbf{p}_a , with $\mathbf{p} = \mathbf{p}_s + \mathbf{p}_a$. It can be verified straightforwardly that

$$\mathbf{p}_a = \sum_{\gamma\beta} \hat{\gamma} C_{\gamma\beta} (\mathbf{S}_a \times \mathbf{S}_b)_\beta, \quad (\text{A3})$$

where

$$\begin{aligned} C_{\gamma x} &= B_{\gamma yz}^a, \\ C_{\gamma y} &= B_{\gamma zx}^a, \\ C_{\gamma z} &= B_{\gamma xy}^a. \end{aligned} \quad (\text{A4})$$

Clearly $\mathbf{p}_a = \mathbf{0}$ for collinear spins, and (A3) for \mathbf{p}_a is the same form as (8) for \mathbf{p} .

Now consider the symmetric component. Setting $\mathbf{S}_a = \pm \mathbf{S}_b$, we have

$$\mathbf{p}_s = \pm \sum_{\gamma\nu\mu} \hat{\gamma} B_{\gamma\nu\mu}^s S_{a\nu} S_{a\mu}. \quad (\text{A5})$$

Choosing \mathbf{S}_a , in turn, along the x, y, z directions, and in the xy, yz, zx planes, one sees that

$$\mathbf{p}_s = \mathbf{0} \text{ for all } \mathbf{S}_a \text{ implies } \mathbf{B}_{\gamma\nu\mu}^s = \mathbf{0} \text{ for all } \gamma, \nu, \mu. \quad (\text{A6})$$

This then proves that (8) uniquely embodies the idea of canted-spin-caused electric dipoles (within the assumption of a bilinear form). It also implies that for any moment resulting from the symmetric component, any canting is incidental, i.e., nonessential.

APPENDIX B: SIMPLE MICROSCOPIC MODEL FOR CANTED-SPIN-CAUSED ELECTRIC DIPOLE

The basic model for the calculations in Ref. 11, generalized to arbitrary symmetry of the bond plus its surroundings (“the crystal”), is presented here. Illustration of its use for checking the abstract symmetry and propagation operations is given.

We consider two essentially one-electron atoms, e.g., two hydrogens or two lithiums. The generalization to two different alkali atoms is not difficult, but for simplicity is not given here.

There are eight spatial wave functions in the basis, an s and three p states for each atom. The average spins on each site (A and B as in Fig. 1) are fixed so that the one-electron basis has just eight states. We write these as

$$s_a \chi_a, s_b \chi_b, p_{av} \chi_a, p_{bv} \chi_b, v = x, y, z,$$

where χ_a and χ_b are the spin states. The spatial parts are assumed to be Wannier functions, i.e., they are hybridized to make them mutually orthogonal (the overlaps of atomic orbitals are assumed small). We denote the two s states as $\phi_i, i = 1, 2$, and the remaining states as $\phi_i, i = 3, \dots, 8$. So each unperturbed atom has two energies, the s state and the p state, separated by $\Delta_0 > 0$. The model Hamiltonian is

$$H = \Delta_0 \sum_{i=3}^8 n_i + \left(\sum_{i \leq 2, j > 2} \tilde{v}_{ij} c_i^\dagger c_j + \text{H.c.} \right) + U \sum_{\text{on-site}} n_i n_j. \quad (\text{B1})$$

Here $n_i = c_i^\dagger c_i$ and $\tilde{\sum}$ means to sum only over terms where i and j refer to different sites. Sample terms are $\langle s_a \chi_a | v | p_{bv} \chi_b \rangle$. v is the spin-orbit coupling operator

$$v = a_0 \nabla V \times \tilde{\mathbf{p}} \cdot \mathbf{s}, \quad (\text{B2})$$

where V (which appears in Ref. 36) is an effective potential energy that reflects the crystal symmetry excluding magnetic ordering and spin-orbit coupling, a_0 involves only fundamental constants, and $(\tilde{\mathbf{p}}, \mathbf{s}) = (\text{momentum}/\hbar, \text{spin}/\hbar)$.

In fact, the one-electron operator (B2) is an approximation to the actual spin-orbit coupling, which is a rather complicated two-electron operator.⁴⁵ There is a considerable literature attempting to calculate SO effects in various approximation schemes, e.g., the Hartree-Fock approximation^{46–48} considering single atoms, a different mean-field approximation⁴⁹ applicable to many-center systems. The latter found that a local potential gave excellent results for g tensors in certain molecules (although in the best approximation V is nonlocal). The simplest approximation that we found in the literature used the Coulomb or Hartree term for $V(\mathbf{r})$.⁴⁴ We explicitly make use of locality, and the only property important for the present considerations is that it be true to the symmetry of the system studied.

Because the spin-orbit term includes only transitions, $s_a \rightarrow p_{bv}$ and $s_b \rightarrow p_{av}$ between the two sites, we call this intersite spin-orbit coupling.

The unperturbed ground state for the system is

$$\Phi_0 = c_1^\dagger c_2^\dagger |0\rangle. \quad (\text{B3})$$

To first order, the perturbed ground state is

$$\Phi = \Phi_0 - \Delta^{-1} \sum_{i \leq 2, j > 2} \tilde{v}_{ji} c_j^\dagger c_i \Phi_0, \quad (\text{B4})$$

where $\Delta = \Delta_0 + U$. Measuring \mathbf{r} from the midpoint of the bond, it is easily shown that $\langle \Phi_0 | \mathbf{r}_1 + \mathbf{r}_2 | \Phi_0 \rangle = 0$, so that the electric dipole moment

$$\begin{aligned} \mathbf{p} &= e \langle \Phi | \sum_{ij} \langle \phi_i | \mathbf{r} | \phi_j \rangle c_j^\dagger c_i | \Phi \rangle \\ &= -\frac{e}{\Delta} \sum_{i \leq 2, j > 2} \tilde{v}_{ji} \langle i | \mathbf{r} | j \rangle + \text{c.c.} \end{aligned} \quad (\text{B5})$$

to leading order. In terms of the explicit one-electron states, this is

$$\mathbf{p} = -\frac{e}{\Delta} \sum_v \langle p_{av} \chi_a | v | s_b \chi_b \rangle \langle s_b \chi_b | \mathbf{r} | p_{av} \chi_a \rangle + (a \leftrightarrow b) + \text{c.c.} \quad (\text{B6})$$

We have

$$\begin{aligned} \langle p_{av} \chi_a | v | s_b \chi_b \rangle &= -i a_0 \langle p_{av} | \nabla V \times \nabla | s_b \rangle \\ &\quad \times \langle \chi_a | \mathbf{s} | \chi_b \rangle, \\ \langle s_b \chi_b | \mathbf{r} | p_{av} \chi_a \rangle &= \langle s_b | \mathbf{r} | p_{av} \rangle \langle \chi_b | \chi_a \rangle. \end{aligned} \quad (\text{B7})$$

With

$$\begin{aligned} \mathbf{u} &\equiv \langle \chi_a | \mathbf{s} | \chi_b \rangle, \\ w &\equiv \langle \chi_a | \chi_b \rangle, \end{aligned} \quad (\text{B8})$$

and Eq. (B7), Eq. (B6) becomes

$$\mathbf{p} = -2a_0 \frac{e}{\Delta} \sum_v \langle p_{av} | \nabla V \times \nabla s_b \rangle \cdot \text{Im}(\mathbf{u}w^*) \langle s_b | \mathbf{r} | p_{av} \rangle + (a \leftrightarrow b). \quad (\text{B9})$$

With the help of the well-known equations for χ_c such that the average in χ_c , $\langle \mathbf{s} \rangle_c \equiv \mathbf{S}_c$ points in the direction with polar angles θ_c, ϕ_c , one can show that

$$\text{Im}(\mathbf{u}w^*) = -\mathbf{S}_a \times \mathbf{S}_b. \quad (\text{B10})$$

We then obtain

$$\mathbf{p} = 2a_0 \frac{e}{\Delta} \sum_v [\langle s_b | \mathbf{r} | p_{av} \rangle \langle p_{av} | \nabla V \times \nabla s_b \rangle - (a \leftrightarrow b)] \cdot \mathbf{S}_a \times \mathbf{S}_b. \quad (\text{B11})$$

Choose the p functions as

$$\begin{aligned} p_{av} &= v p_a, \quad v = y, z, \\ p_{bv} &= v p_b, \quad v = y, z, \\ p_{ax} &= (x + 1/2) p_a, \\ p_{bx} &= (x - 1/2) p_b, \end{aligned} \quad (\text{B12})$$

where p_a, p_b are spherically symmetric about points A, B , respectively. Define

$$\mathbf{T}_{ba}^v \equiv \langle s_b | \mathbf{r} | p_{av} \rangle = \hat{v} T_{ba}^v. \quad (\text{B13})$$

The last equality follows from the cylindrical symmetry of $s_b(\mathbf{r}) p_a(\mathbf{r})$. Further,

$$\begin{aligned} T_{ba}^v &= \langle s_b | v^2 p_a \rangle = T_{ab}^v \quad \text{for } v = y, z, \\ T_{ba}^x &= \langle s_b | x(x + 1/2) p_a \rangle = T_{ab}^x. \end{aligned} \quad (\text{B14})$$

These results follow from $p_{av}(-x, y, z) = p_{bv}(x, y, z)$ for $v = y, z$ and $p_{ax}(-x, y, z) = -p_{bx}(x, y, z)$. Hence the quantity $\langle s_b | \mathbf{r} | p_{av} \rangle$ factors out of the square brackets in (B11).

Comparison of (B11) with (8) shows that, to within the constant factor $2a_0 e / \Delta$, the basic matrix defined in the general theory (8) is

$$\begin{aligned} C_{v\mu} &= T_{ba}^v [\langle p_{av} | (\nabla V \times \nabla)_\mu s_b \rangle - (a \leftrightarrow b)] \\ &\equiv T_{ba}^v (I_{ab}^{v\mu} - I_{ba}^{v\mu}) \end{aligned} \quad (\text{B15})$$

for the present detailed microscopic model.

Let us first check the fundamental result (27) that $C_{v\mu}$ is invariant under inversion. We calculate C' , the inverted $C_{v\mu}$, by replacing $V(\mathbf{r})$ by $V' = V(-\mathbf{r})$. Consider, e.g.,

$$\begin{aligned} C'_{xx} &= T_{ba}^x \left[\int d^3r p_{ax} \right. \\ &\quad \left. \times \left(\frac{\partial V'}{\partial y} \frac{\partial s_b}{\partial z} - \frac{\partial V'}{\partial z} \frac{\partial s_b}{\partial y} \right) - (a \leftrightarrow b) \right]. \end{aligned} \quad (\text{B16})$$

On changing the integration variables, $\mathbf{r} \rightarrow -\mathbf{r}$, $V' \rightarrow V$, and $I_{ab}^{xx} \rightarrow -I_{ba}^{xx}$, so that $C'_{xx} = T_{ba}^x (-I_{ba}^{xx} + I_{ab}^{xx})$, which is C_{xx} . The property $p_{ax}(-x, y, z) = -p_{bx}(x, y, z)$ was essential to the conclusion.

Now consider checking some of the symmetry rules corresponding to Moriya's five symmetry operations.

Rule 1. $C_{v\mu}$ does not change under inversion whether or not the system is invariant under inversion, as was just shown. Hence the general conclusion, namely that inversion symmetry places no restriction on C , is verified for the model.

Rule 2. Here $V(x, y, z) = V(-x, y, z)$. Thus, e.g., in C_{xx} the integral $I_{ab}^{xx} = -I_{ba}^{xx}$, seen by changing the integration variable x to $-x$, returning the initial expression. That is, this symmetry puts no restriction on C_{xx} . Next,

$$\begin{aligned} C_{xy} &= T_{ba}^x \left[\int d^3r p_{ax} \left(\frac{\partial V}{\partial z} \frac{\partial s_b}{\partial x} - \frac{\partial V}{\partial x} \frac{\partial s_b}{\partial z} \right) - (a \leftrightarrow b) \right] \\ &= T_{ba}^x (I_{ba}^{xy} - I_{ab}^{xy}) = -C_{xy}. \end{aligned} \quad (\text{B17})$$

(One sees that $I_{ab}^{xy} = I_{ba}^{xy}$.) Therefore, $C_{xy} = 0$. Thus the model has verified two of the matrix elements in (12), deduced earlier by a general, model-independent, symmetry argument. These examples should suffice to illustrate the procedure, which can be seen to check all the previous results.

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