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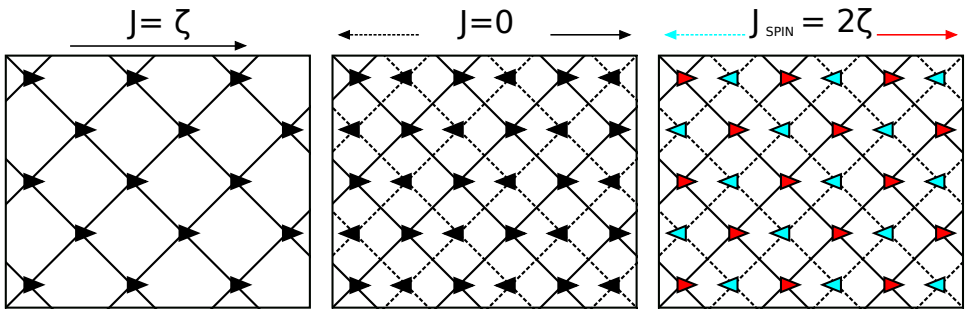
Abstract

Here we predict the existence of a linear bulk spin photovoltaic effect, where spin currents are produced in antiferromagnetic materials as a response to linearly polarized light, and we describe the symmetry requirements for such a phenomenon to exist. This effect does not depend on spin-orbit effects or require inversion symmetry breaking, distinguishing it from previously explored methods. We propose that the physical mechanism is the nonlinear optical effect "shift current," and calculate from first principles the spin photocurrent for hematite and bismuth ferrite. We predict a significant response in these materials, with hematite being especially promising due to its availability, low band gap, lack of charge photocurrents, and negligible spin orbit effect.



(a) (b) (c)

FIG. 1. A non-centrosymmetric lattice, like the one shown in (a), will generally exhibit the bulk photovoltaic effect. When a copy of the lattice related by mirror symmetry is added, shown in (b), the total current will be zero. However, if the two sublattices have opposite spin, represented dichromatically in (c), a pure spin current will result.

Spintronics - the use of electronic devices relying on the manipulation of spin rather than charge - promises to play an important role in the development of future electronic and computing devices [1]. However precise control of electron spin, including the generation of spin filtered currents, presents a difficult challenge. There are four main mechanisms for spin current generation currently known: spin-Hall effects [2–4], illumination with circularly polarized light [5–8], subband splitting due to spin-orbit coupling [9–13], and, recently, the spin-Seebeck effect [14]. While pure spin current generation has been achieved using linearly polarized light, the subband splitting created by spin-orbit effects is required, along with strong inversion symmetry breaking, which constrains the strength of the response. In this work we add a new mechanism: spin separation in antiferromagnets by linearly polarized light. Neither spin-orbit coupling nor inversion symmetry breaking is required, making entirely distinct classes of materials candidates for application.

Previously, we reported on first principles calculations of the bulk photovoltaic effect in ferroelectric materials [15]. The bulk photovoltaic effect is a third rank tensor and is restricted to 20 of the 21 non-centrosymmetric groups. One can consider up and down spin electrons separately, but in the presence of time reversal symmetry and negligible spin-orbit interaction, these are required to respond identically, and only charge currents are generated. However, when antiferromagnetic materials are considered, a new possibility emerges. The spin centers may produce opposite responses to the illumination, generating a net charge current of zero, and a net spin current.

This is illustrated by the 2D toy system in Fig. 1. Shown in (a) is a square lattice decorated by triangles. The lattice breaks inversion symmetry, and in general will produce a bulk photovoltaic response. However, suppose we add as a sublattice a duplicate of the original lattice, related to it by a symmetry operation. In (b) this is shown for a mirror symmetry. The additional sublattice will produce a bulk photovoltaic response that is the mirror of the response of the first lattice, canceling it. If, however, we turn on opposite spins for the two sublattices, as indicated by the coloring in (c), the currents produced by the two lattices will have opposite spin, resulting in pure spin current.

The procedure for determining the crystal classes that allow for this effect is similar to that for the charge bulk photovoltaic effect; however, the Shubnikov group – specifically, the black-and-white, or dichromatic group [16] – must be used instead of the space group. Shubnikov groups consist of the space group operations, a subset of which are multiplied an additional operation of antisymmetry. It is important to note that these are distinct from double groups. The unit cell is divided into sections of two types, often denoted as "black" or "white", which interchange upon application of antisymmetry. In this case, our black/white are spin up/down, so the antisymmetry operation can be identified with time reversal. As seen in Fig. 1 above, the crystal may be antisymmetric under a given symmetry operation (*e.g.* inversion), but if the time reversal operator is applied, the combined operation is a member of the symmetry group. Formally,

$$M = H + \theta(G - H)$$

Where M is the magnetic group, θ is the time reversal operation, G is the space group of the lattice, and H is the invariant subgroup of G that respects spin symmetry.

Each magnetic group has a principal representation analogous to the operation possessing the full symmetry of the crystal when magnetic ordering is excluded. Only tensor elements or linear combinations thereof that belong to this principal representation are allowed to be nonzero. For a third rank tensor, this requires that the representation generated by taking the cube of the vector representation contain the principal representation.

Since the symmetry of a tensor is dependent only on a space group's isogonal point group, we restrict our analysis to the point groups. The magnetic groups that derive from a given point group can be determined from the parent point group's character table: for each invariant subgroup H there is a one dimensional representation that has positive character for

the operations in H only and becomes the principal representation of the magnetic group. The character tables for these child magnetic groups can be determined, but since we are only interested in the principal representation, we need only the monochromatic group tables to identify the representation associated with reduction of symmetry to H. However, one additional consideration must be made: the magnetic group must also be able to host antiferromagnetism. In some cases, the magnetic point group will not admit antiferromagnetism, but a non-symmorphic space group for which the point group is isogonal can. Using this we can identify all the dichromatic groups that allow the spin photovoltaic effect. Further analysis can reveal which tensor elements belong to the principal representation. Fortunately, this has already been performed for the piezomagnetic effect, which has identical symmetry properties [16].

We propose that these spin currents will be generated by the "shift current" mechanism [17, 18]. Shift current is an intrinsic photovoltaic effect produced by the second-order interaction with light in non-centrosymmetric materials. Briefly, the current can be described by the equation

$$\begin{aligned} J_q &= \sigma_{rsq} E_r E_s \\ \sigma_{rsq}(\omega) &= \pi e \left(\frac{e}{m\hbar\omega}\right)^2 \sum_{n',n''} \int \mathrm{d}\mathbf{k}\ \left(f[n''\mathbf{k}] - f[n'\mathbf{k}]\right) \\ &\quad \times \langle n'\mathbf{k}|\, \hat{P}_r\, |n''\mathbf{k}\rangle \langle n''\mathbf{k}|\, \hat{P}_s\, |n'\mathbf{k}\rangle \\ &\quad \times \left(-\frac{\partial \phi_{n'n''}(\mathbf{k},\mathbf{k})}{\partial k_q} - [\chi_{n''q}(\mathbf{k}) - \chi_{n'q}(\mathbf{k})]\right) \\ &\quad \times \delta\left(\omega_{n''}(\mathbf{k}) - \omega_{n'}(\mathbf{k}) \pm \omega\right) \end{aligned} \tag{1}$$

where n', n'' index the bands, $\mathbf{k}$ is the wavevector, $\omega_n(\mathbf{k})$ is the energy of the nth band, and σ_{rsq} is the current-field response tensor. ϕ and χ represent the momentum element phases and Berry connections, respectively. The expression has the form of a Fermi's Golden Rule transition rate multiplied by a term with units of distance called the shift vector, which appears on the fourth line of 1. The phenomenon is distinct from other photovoltaic effects; rather than excited carriers being split by an electric field, current is produced by coherent excitations that have themselves a non-zero net momentum. This momentum is a function of the reciprocal lattice vector, and therefore must reflect the symmetry of the Brillouin zone. Thus, while the preceding symmetry argument demonstrates that a spin photovoltaic effect

may exist in principle, the unique properties of the shift current suggest it as a mechanism by which such an effect can physically manifest.

In the case of a spin-polarized system, the calculation is performed for spin up and spin down bands separately, so that

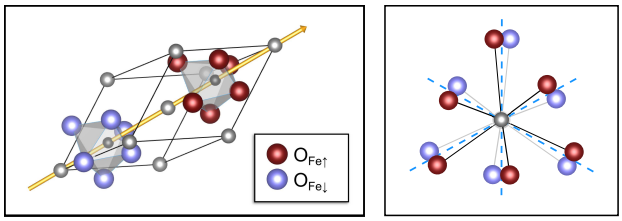
$$
\begin{aligned}
\sigma^{\mathrm{S}}_{rsq}(\omega) &= \sigma_{rsq,\uparrow}(\omega) - \sigma_{rsq,\downarrow}(\omega) \\
\sigma_{rsq,\uparrow/\downarrow}(\omega) &= \pi e \left(\frac{e}{m\hbar\omega}\right)^2 \sum_{n',n''} \int \mathrm{d}\mathbf{k} \\
&\quad \left(f[n''_{\uparrow/\downarrow}\mathbf{k}] - f[n'_{\uparrow/\downarrow}\mathbf{k}]\right) \\
&\quad \times \left\langle n'_{\uparrow/\downarrow}\mathbf{k}\right| \hat{P}_r \left|n''_{\uparrow/\downarrow}\mathbf{k}\right\rangle \left\langle n''_{\uparrow/\downarrow}\mathbf{k}\right| \hat{P}_s \left|n'_{\uparrow/\downarrow}\mathbf{k}\right\rangle \\
&\quad \times \left(-\frac{\partial \phi_{n'_{\uparrow/\downarrow} n''_{\uparrow/\downarrow}}(\mathbf{k},\mathbf{k})}{\partial k_q} \right. \\
&\qquad\qquad \left. - \left[\chi_{n''_{\uparrow/\downarrow} q}(\mathbf{k}) - \chi_{n'_{\uparrow/\downarrow} q}(\mathbf{k})\right] \right) \\
&\quad \times \delta\left(\omega_{n''_{\uparrow/\downarrow}}(\mathbf{k}) - \omega_{n'_{\uparrow/\downarrow}}(\mathbf{k}) \pm \omega\right)
\end{aligned}
\tag{2}
$$

It is evident that the symmetry effects above are introduced through the intrinsic symmetry of the supplied electronic states, so that Eq. 2 is general; with the addition of time reversal symmetry it reduces to Eq. 1.

The numerical implementation of shift current calculations was described previously in Ref. [15]. The wavefunctions used for the response calculations were generated using the Quantum ESPRESSO package at the level of density functional theory with the generalized gradient approximation [24]. Due the well-known inability of DFT to model Mott insulator systems correctly, Hubbard U terms were added for hematite [19] and BFO [21]. Norm-conserving, designed non-local pseudopotentials were produced using the OPIUM package [25, 26]. Charge densities were generated on 8×8×8 k-point grids and used to generate wavefunctions on finer grids as necessary.

We have computed the spin photovoltaic response for the well-known antiferromagnets NiO, Fe_2O_3 (hematite), and the multiferroic $BiFeO_3$ (BFO).

The magnetic group for NiO derives from the $A_{2\mathrm{u}}$ representation of point group O_h. There are no third rank tensor elements that belong to this representation, so the crystal will have no spin bulk photovoltaic effect. Calculations were performed and confirm the absence of any response.

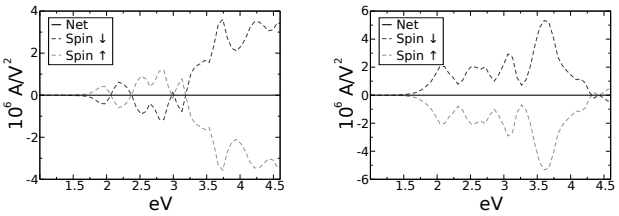


(a) (b)

FIG. 2. (a) shows the primitive unit cell for BFO, with the oxygen cages colored according to the spin of the iron atoms they enclose. Hematite takes a very similar structure, with iron in place of bismuth and no ferroelectric distortion. (b) shows the oxygen cages viewed along the polarization direction. The mirror components of the glide planes are shown by the blue dashed lines. From this view it is clear that reversing the distortion of the oxygen cages has the same effect as inverting the spins; the current generated under one oxygen cage distortion is the mirror of that generated by the opposite distortion, leading to spin current along the X axis. There may also be charge current in other directions depending on the symmetry, as in BFO.

Hematite [19] has space group 167, with point group D_{3d}, while BFO has space group 161, with point group C_{3v}. The two materials both take the ilmenite structure, with BFO, shown in Fig. 2(a), experiencing a ferroelectric distortion. It is worth noting that inversion symmetry will kill any charge bulk photovoltaic effect in hematite, whereas BFO has been demonstrated to have a large bulk photovoltaic effect [20, 21]. In both cases the magnetic group is associated with the reduction to C_3 symmetry, deriving from the representations A_{2g}(hematite) and A_2(BFO), so that a glide plane relates the up and down spins. As is evident in Fig. 2(b), which shows the oxygen cages viewed along the material polarization direction, the environments of these two spin centers differ by the direction of distortion of the coordinating oxygen atoms, converting what would otherwise be a mirror symmetry to a glide plane, and introducing a chirality into the structure. This is crucial, as it ensures that flipping the spins switches chirality, allowing a spin current to exist.

We note that bismuth ferrite possesses significant spin-orbit coupling which introduces spin canting and weak ferromagnetism. While the photovoltaic response calculation can be be performed with the full spinorial wavefunctions without much difficulty, in the presence of large spin-orbit interaction the result no longer conforms to a rigorous definition of spin current [22]. However, in the present context the effect is relatively small, so for our calculation



(a) (b)

FIG. 3. (a) displays the spin and charge current spectra for hematite in direction xxX (σ^{S}_{11}) and (b) shows the spectra in zxY (σ^{S}_{14}). The total charge currents vanish in all directions for hematite.

we impose antiferromagnetic ordering, and compute the spin current for this approximation to the spin structure.

Tensor elements that are antisymmetric under the glide plane operation survive, and are

$$\sigma_{\mathrm{hematite}} = \begin{bmatrix} \sigma^{\mathrm{S}}_{11} & -\sigma^{\mathrm{S}}_{11} & 0 & \sigma^{\mathrm{S}}_{41} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sigma^{\mathrm{S}}_{41} & -\sigma^{\mathrm{S}}_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{3}$$

for hematite, and

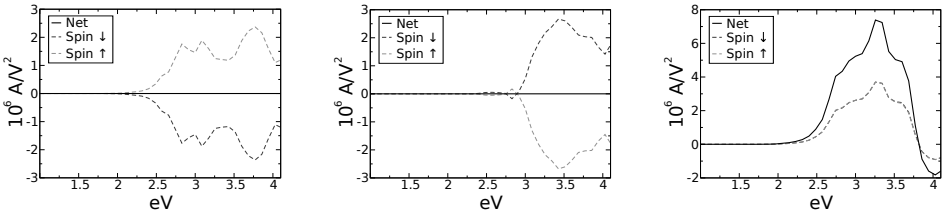
$$\sigma_{\mathrm{BFO}} = \begin{bmatrix} \sigma^{\mathrm{S}}_{11} & -\sigma^{\mathrm{S}}_{11} & 0 & \sigma^{\mathrm{S}}_{41} & \sigma_{52} & -\sigma_{22} \\ -\sigma_{22} & \sigma_{22} & 0 & \sigma_{52} & -\sigma^{\mathrm{S}}_{41} & -\sigma^{\mathrm{S}}_{11} \\ \sigma_{13} & \sigma_{13} & \sigma_{33} & 0 & 0 & 0 \end{bmatrix} \tag{4}$$

for BFO, with charge photovoltaic response elements included for completeness.

The spectra for the unique elements are shown for hematite in Fig. 3, and for BFO in Fig. 4, with the charge photovoltaic response for comparison. The spin response for both materials is of a similar magnitude to the charge response of BFO, indicating that it should be easily observable.

We consider hematite to be the preferred material for measuring the spin bulk photovoltaic effect, as it cannot produce charge photocurrents, is uncomplicated by spin-orbit effects, and has a lower band gap and is more readily available than BFO.

We have described a new mechanism for large pure spin currents in antiferromagnetic materials in response to linearly polarized light and have elucidated the symmetry requirements for materials to possess a nonzero response. We predict that the well-known antiferromagnets hematite and bismuth ferrite can produce large pure spin currents. This method is not



(a) (b) (c)

FIG. 4. Spin and charge photovoltaic tensor elements for $BiFeO_3$ in the xxX direction ($\sigma^{\rm S}_{11}$) and the zxY direction ($\sigma^{\rm S}_{14}$) are shown in (a) and (b). Compared with them is the charge current in yyY direction (σ_{22}).

dependent on the strength of spin-orbit splitting or inversion symmetry breaking [10, 12, 23], representing a distinct mechanism that complements existing methods for producing pure spin current. Given hematite's low band gap of 2.2 eV, easily accessible by visible illumination, we expect that this new effect can be observed experimentally.

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