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Canonical magnetic insulators with isotropic magnetoelectric coupling

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We have performed a systematic representation-theory-based search for the simplest structures allowing isotropic magnetoelectric coupling. We find 30 such structures, all sharing a common pattern of atomic displacements in the direction of atomic magnetic moments. We focus on one of these 30 canonical structures and find that it is generically realized in a class of fractionally substituted pyrochlore compounds with an all-in-all-out magnetic order. Furthermore, we find that these substituted pyrochlore compounds have a substantial Chern-Simons orbital magnetoelectric component ($\theta = 0.1$–0.2). While this component is also formally present in strong Z_2 topological insulators ($\theta = \pi$), its effects are observable there only if time-reversal symmetry is broken at the surface.

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One of the characteristics of the interplay between electric and magnetic degrees of freedom is a linear magnetoelectric tensor α_{ij}. It expresses the *electric* polarization P_i induced in an insulator by an applied *magnetic* field B_j. Such a response requires broken time-reversal and inversion symmetries, and is known to occur in some compounds such as Cr_2O_3. In general, the tensor $\alpha_{ij} = \partial P_i/\partial B_j$ has nine independent coefficients. From the symmetry point of view the simplest possible tensor α_{ij} is diagonal, with all elements on the diagonal being equal,

$$\alpha_{ij} = \alpha^{\rm iso}\delta_{ij} = \begin{pmatrix} \alpha^{\rm iso} & 0 & 0 \\ 0 & \alpha^{\rm iso} & 0 \\ 0 & 0 & \alpha^{\rm iso} \end{pmatrix}. \quad (1)$$

Materials with such an isotropic magnetoelectric (ME) response have been discussed in the literature,[1–3] but such materials still need to be reported experimentally.

Recently, the interest in isotropic ME response has grown sharply due to the discovery[4,5] of a mechanism giving rise to a purely isotropic ME coefficient, and the relationship of this finding to the physics of strong Z_2 topological insulators.[4–7] This component $\alpha^{\rm CS}$ of the ME response is referred to as the Chern-Simons orbital ME polarizability (CSOMP) and is conventionally measured in terms of the dimensionless parameter θ via

$$\alpha^{\rm CS}_{ij} = \theta \frac{e^2}{2\pi h}\delta_{ij}. \quad (2)$$

Here e is the electron charge and h is Planck's constant. In what follows we denote the entire isotropic ME response as $\alpha^{\rm iso}$, and its Chern-Simons component as $\alpha^{\rm CS}$. In strong Z_2 topological insulators, formally $\theta = \pi$ and $\alpha = \alpha^{\rm iso} = \alpha^{\rm CS} = e^2/2h$, but this ME coupling is observable only if the surfaces and interfaces of the sample are consistently gapped by some time-reversal-breaking perturbation.[5,8,9] In Cr_2O_3 and other conventional magnetic insulators, on the other hand, α is easily observable but $\alpha^{\rm CS}$ is small. We seek here a material where $\alpha^{\rm CS}$ is both large and observable, as might be the case in a magnetic insulator that is close to being a strong Z_2 topological insulator.[9]

A critical consideration which determines which of the nine components of α_{ij} can be nonzero is that of symmetry.[10] In many known magnetic insulators, symmetry allows only off-diagonal components of α_{ij} to be nonzero, as, for example, in Li(Fe,Co,Ni)PO_4 and many other compounds which have only α_{xy} and α_{yx} different from zero. Similarly, the series of compounds (Tb,Dy,Ho)PO_4 have $\alpha_{xx} = -\alpha_{yy}$ as the only two nonzero components. On the other hand, some compounds such as Cr_2O_3 have a diagonal α of the form $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$, which is only isotropic if artificially tuned to be so. However, in Cr_2O_3 one expects the response along the rhombohedral axis α_{zz} to arise from a different microscopic mechanism than the α_{xx} and α_{yy} components, since the spin moments on the Cr atoms are aligned along the $\pm z$ direction and can easily tilt towards the x-y plane.[11,12]

The three main contributions of this Rapid Communication are as follows. First, we find an exhaustive list of the 30 simplest crystal structures and corresponding arrangements of magnetic moments which, by symmetry, allow a purely isotropic linear ME coupling $\alpha^{\rm iso} = \alpha_{xx} = \alpha_{yy} = \alpha_{zz}$. Second, using density-functional theory (DFT) calculations we find that one of these 30 cases is generically realized in any member of a class of substituted pyrochlore compounds with all-in-all-out magnetic order. Third, we find a relatively large CSOMP component ($\alpha^{\rm CS} = 0.85$–1.62 ps/m) from our calculations on these substituted pyrochlore compounds.

We start with an analysis of the required symmetry breaking which would allow for an isotropic linear ME coupling. Let us first consider the effects of symmetry operations on the isotropic ME coupling coefficient $\alpha^{\rm iso}$ defined in Eq. (1). The real number $\alpha^{\rm iso}$ must change sign both under the time-reversal transformation (since it transforms B_j into $-B_j$) and under the inversion transformation (since it transforms P_i into $-P_i$). Furthermore, $\alpha^{\rm iso}$ is unchanged under rotation (since it measures an isotropic response) or translation (since it is a bulk response). Therefore, there are two classes of transformations which change the sign of $\alpha^{\rm iso}$. The first class (class T) of transformations consists of the time-reversal operator either by itself or followed by a proper rotation and/or a translation. The second class (class P) of transformations consists of the inversion symmetry either by itself or followed by a proper rotation and/or a translation. Therefore, any system with at least one symmetry operation in either class T or P is excluded as a candidate for an isotropic ME material.

Consider the example of a simple cubic (primitive) lattice with one atom per unit cell, and a magnetic moment on that atom pointing along the z axis. Such a system has broken time-reversal symmetry. However, time-reversal symmetry followed by a twofold rotation around the x axis will still be a symmetry (class T), and it will enforce $\alpha^{\rm iso} = 0$. (In fact, in this simple example, even inversion symmetry would enforce $\alpha^{\rm iso} = 0$.) Therefore, as mentioned earlier, it is clear that not every magnetic order has the correct symmetry to produce a nonzero isotropic ME coupling.

We now search for the highest-symmetry atomic structures with the property that the isotropic linear ME coupling ($\alpha^{\rm iso}$) is allowed by symmetry, i.e., no symmetry elements of the system belong to either class T or P. In other words, such a structure has only those symmetry-breaking perturbations which are essential to allow $\alpha^{\rm iso} \neq 0$. We start our search by selecting a set of the simplest periodic arrangements of atoms (ignoring their magnetic moments for now). We consider all 36 space groups in the cubic system (T, T_h, T_d, O, and O_h point groups) and their 308 Wyckoff orbits (symmetry-related subsets of atoms). For simplicity we only consider Wyckoff orbits with at most one free parameter (227 out of 308). Furthermore, we only consider characteristic[13] orbits (whose symmetry is not larger than that of an underlying space group), leaving us with 62 orbits out of 227.

We now take each of these 62 highest-symmetry periodic arrangements of atoms, and consider all possible arrangements of atomic magnetic moments that do not enlarge the chemical unit cell. Such an arrangement of magnetic moments is described by N magnetic-moment vectors, or equivalently, $3N$ Cartesian variables, where N is the number of sites in the Wyckoff orbit. We construct a $3N \times 3N$ matrix for each symmetry operator in the space group, taking into account the axial nature of the magnetic moment (no sign change under inversion). Using standard space-group character tables we can decompose these $3N \times 3N$ matrices into irreducible representations.[14] Next, we consider all one-dimensional real irreducible representations which satisfy our symmetry constraint, namely, the characters are $+1$ or -1 for symmetry operators with positive or negative determinant (proper or improper rotations), respectively. In other words, such an arrangement of magnetic moments is symmetric under proper rotations, and is symmetric under improper rotations only when coupled with a time-reversal operation.

As a result of this search, we find that 30 of the 62 structures yield a unique periodic arrangement of atoms with magnetic moments satisfying our constraints, while the remainder yield none. These 30 are the simplest (canonical) arrangements of atoms and corresponding magnetic moments allowing for a purely isotropic linear ME coupling. All 30 of these arrangements are listed in the Supplemental Material.[15]

Analyzing these 30 cases, we find two common features. First, we find a *local* motif in which atoms are displaced away from higher-symmetry locations (as described by a single free Wyckoff parameter) and magnetic moments point in the same direction as the displacements. Second, we find that this local motif is arranged in an appropriate three-dimensional network of polyhedra (*global* consistency). Finally, we find that the atomic displacements cause breathing of these polyhedral networks so as to increase the size of half of the polyhedra and decreases the size of the other half.

The magnetic part of this motif, with moments pointing all-in and all-out in neighboring polyhedra, is not very difficult to realize in nature. For example, such a magnetic order has been suggested in a variety of pyrochlores with magnetic Os, Ir, or rare-earth atoms, and was first predicted theoretically in Ref. 16. A well-known example is $Cd_2Os_2O_7$, which is experimentally found to be consistent with a long-range all-in-all-out magnetic order on the Os site as shown in Refs. 17 and 18 and in theoretical calculations in Ref. 19. Similarly, all-in-all-out magnetic order occurs on the Ir site in $Eu_2Ir_2O_7$ as shown in Ref. 20 and on both Nd and Ir sites in $Nd_2Ir_2O_7$ as shown in Ref. 21. Thus, we may achieve the desired isotropic magnetoelectric coupling if we can augment the observed noncollinear spin ordering with an appropriately similar pattern of atomic displacements.

With this motivation, in the remainder of this Rapid Communication we focus on just one of our 30 structures, namely, the one having space group $F\bar{4}3m$, Wyckoff orbit 16e, and magnetic moments corresponding to the irreducible representation Γ_2 (structure 13 in the Supplemental Material[15]). The coordinates[22] of the atoms in this Wyckoff orbit are (u,u,u), $(u,-u,-u)$, $(-u,u,-u)$, and $(-u,-u,u)$, with an arbitrary value of the real number parameter u. The directions of the magnetic moments in the Γ_2 representation are $(1,1,1)$, $(1,-1,-1)$, $(-1,1,-1)$, and $(-1,-1,1)$, respectively. In the special case that $u = 1/8$ (or equivalently $3/8$, $5/8$, or $7/8$) the symmetry increases from $F\bar{4}3m$ to $Fd\bar{3}m$, the Wyckoff orbit notation changes to 16c or 16d, and the ME coupling is forced to zero by symmetry. Such an arrangement corresponds to a network of corner-sharing tetrahedra as formed for example by the A or B sites of the pyrochlores $A_2B_2O_7$ or the B sites of spinels AB_2O_4. Displacing atoms away from $u = 1/8$ by taking $u = 1/8 + \epsilon$ for some small ϵ leads to a breathing distortion of the tetrahedral network, with half of the tetrahedra increasing in size and the other half shrinking (see red versus blue tetrahedra in Fig. 1). The direction of each atomic displacement is the same as the direction of the corresponding local magnetic moment in the Γ_2 representation (the so-called all-in-all-out magnetic arrangement shown by the arrows in Fig. 1).

We now focus on a realization of this particular canonical structure in a substituted $A_2B_2O_7$ pyrochlore. The compositional formula of the pyrochlores is often written as $A_2B_2O_6O'$ since oxygen atoms occupy two distinct crystallographic sites labeled O and O′, with the O′ sites centered inside the tetrahedra formed by the A lattice. Based on a symmetry analysis of the pyrochlore lattice, we find that if the O′ sites are divided into two regular sublattices, one of which is substituted by a different atom (or a vacancy), the symmetry of the pyrochlore is reduced to $F\bar{4}3m$, with both A and B atoms moved onto 16e Wyckoff orbits. (This does not double the size of the primitive cell.) Therefore, we generically expect that any $A_2B_2O_7$ pyrochlore with all-in-all-out magnetic order on the A sites, the B sites, or both, will become an isotropic ME upon 50% O′ substitution.

Indeed, we confirm these findings using first-principles calculations on two families of pyrochlore compounds. The first

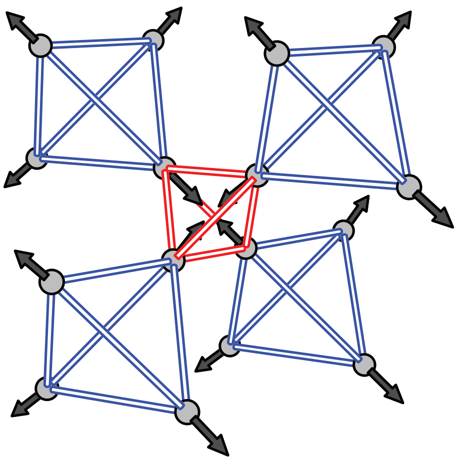

FIG. 1. (Color online) Sketch of one out of 30 canonical structures in which isotropic ME coupling $\alpha^{\rm iso}$ is allowed by symmetry. Atoms (gray spheres) are displaced in the direction of their magnetic moments (arrows). These displacements change the network of corner sharing tetrahedra by shrinking half of the tetrahedra (red) and enlarging the other half (blue).

family we analyzed has nonmagnetic A^{2+} ions and magnetic B^{5+} ions. We find that these compounds have an isotropic ME coupling for any combination of $A =$ (Cd, Zn, Hg), $B =$ (Os, Ru), and $X =$ (S, Se, or Te) substituting half of the O′ sites. (The general formula of such a compound is $A_2B_2O_{6.5}X_{0.5}$.) Using methods from Ref. 9, we have computed θ for $Zn_2Os_2O_{6.5}Te_{0.5}$, using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[23] and an on-site Hubbard U of 3.0 eV (Ref. 24) (we find a negligibly small dependence of θ on U). We obtain $\theta = 0.11$, corresponding to $\alpha^{\rm CS} = 0.85$ ps/m.[25] The band structure of this compound is shown in Fig. 2; the minimum direct and indirect band gaps are 0.39 and 0.25 eV, respectively, and the Os magnetic moment is $0.94\mu_{\rm B}$.

We also find that replacing $B =$ Os with $B =$ Ru roughly doubles θ ($\theta = 0.21$ in $Cd_2Ru_2O_{6.5}Te_{0.5}$, corresponding to $\alpha^{\rm CS} = 1.62$ ps/m). Unfortunately, $B =$ Ru compounds tend to become semimetallic upon Se or Te substitution, at least within the density-functional approximation (here PBE), which often underestimates gaps. However, these compounds may be

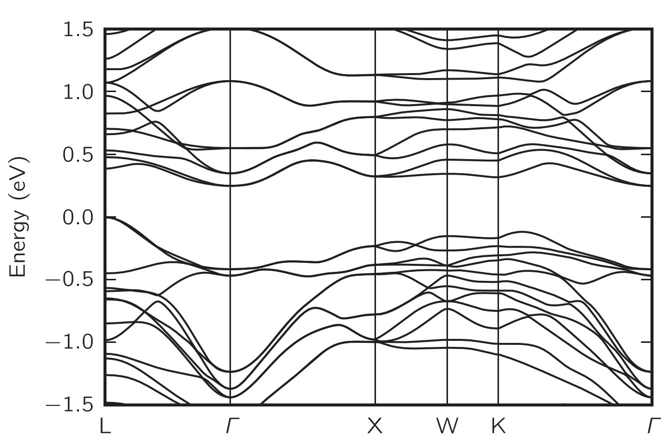

FIG. 2. First-principles fully relativistic computed band structure of $Zn_2Os_2O_7$ with partial Te substitution ($Zn_2Os_2O_{6.5}Te_{0.5}$).

easier to handle experimentally since they do not contain toxic Os. For this first family we find, in general, that swapping the A site from Zn to Cd to Hg somewhat reduces θ, while swapping X from S to Se to Te increases θ.

The second family of pyrochlore compounds that we have analyzed have magnetic ions on both A and B sites, typically rare-earth A^{3+} ions and other B^{4+} ions. Since both ions are magnetic, one might expect larger values of θ than in the first family. Furthermore, magnetism on the A sites is preferred over magnetism on the B sites, since the A site is about two times closer (2.2 Å versus 4.2 Å) to the substituted atom X than the B atom. We have not attempted to calculate the values of θ in these compounds, since it is well known that local DFT approximations do not treat f valence electrons reliably in the rare-earth atoms.

In order to relate our predictions to previous experimental work, we give a brief overview here of known pyrochlore compounds with breathing distortions that can potentially be combined with all-in-all-out magnetic order. We are unaware of any other prediction of a pyrochlore compound in which breathing and magnetism occur at the same time (and the system remains insulating). This is consistent with the spirit of Ref. 26, where it was argued that atomic distortions and magnetic moments tend not to happen on the same atomic site. (At least, this was argued for oxides; it is unclear whether it should also hold for fluorides.[27]) Our proposed mechanism for displacing the magnetic ions in the pyrochlores does not, however, rely on any intrinsic displacive tendency; it is more reminiscent of the case of $BiFeO_3$, where an independent mechanism—Bi off-centering there, O′ replacement here—provides the driving force for magnetic-ion off-centering.

The substitution of the O′ site with sulfur has been analyzed previously in Ref. 28 (and reviewed in Ref. 29) in $Cd_2Nb_2O_{7-x}S_x$ for the entire range $0 < x < 1$ of substitution. While the arguments given above were for the case of a full 50% substitution (complete replacement of a sublattice), note that the same effects will occur, and a nonzero $\alpha^{\rm iso}$ will be generated, if only a partial replacement is carried out by alloying on the O′ site, as long as the concentration is different for the two O′ sublattices. Only polycrystalline $Cd_2Nb_2O_{7-x}S_x$ samples were made, and it is not known whether or not substituted atoms are ordered. However, somewhat suggestive of an ordered state is a finding[28,29] that its structural phase diagram differs for $x < 0.5$ compared to $x > 0.5$, with the $x > 0.5$ case being more complicated. More detailed structural studies have been made on the somewhat related compounds $Pb_2Ir_2O_{6.5}$ in Ref. 30 and $Pb_2Ru_2O_{6.5}$ in Ref. 31. In these compounds, instead of substitution, half of the O′ sites are replaced with vacancies. Detailed structural studies in these compounds show that vacancies are indeed in the long-range-ordered arrangement.[32] Even if the compositional ordering is only short ranged, we point out that the commonly used ME annealing technique can rearrange ME domains in the sample so that each locally ordered region has the same sign of $\alpha^{\rm iso}$. Therefore, it may be enough to require that $A_2B_2O_{6.5}X_{0.5}$ has only locally ordered substituted atoms X.

We leave for future work the analysis of other realizations of this particular canonical structure (Wyckoff orbit 16e in $F\bar{4}3m$ can also appear in spinels), as well as the study of the remaining 29 (out of 30) canonical magnetically decorated structures.

Nevertheless, we point out some interesting candidates among these. For example, chromium boracites $Cr_3B_7O_{13}Br$ and $Cr_3B_7O_{13}I$ are believed to have an antiferromagnetic ground state[33] and may be magnetoelectric.[1] Symmetry lowering of the Cr atoms to Wyckoff orbit $24g$ in group $F23$ would allow $\alpha^{\mathrm{iso}} \neq 0$ (the corresponding characteristic orbit is $24e$ in $Fm\bar{3}m$). The ullmannite structure[34] found in NiSbS (and many other compounds) is also interesting, as it consists of three different atoms on the $4a$ orbit in the space group $P2_13$. Similarly, silicides such as FeSi and MnSi are composed of the same Wyckoff orbit ($4a$ orbit in $P2_13$) and are known to be magnetic.

In summary, our work shows that pyrochlores partially substituted by S, Se, or Te, and having magnetic all-in-all-out magnetic order, generically have a nonzero and purely isotropic linear ME coupling. If such a compound is made in the laboratory, and its ME coupling is measured, this would be a realization of a purely isotropic ME material, and also a material with a substantial[35] ME response resulting from the orbital-electronic mechanism.[36] For example, a value of $\theta = 0.1$, which was shown above to be quite plausible, would make the orbital magnetoelectic coupling comparable to the entire (spin-ion dominated) response in Cr_2O_3. Furthermore, such a compound would have substantial Chern-Simons ME polarizability, which is formally present in strong Z_2 topological insulators as well, but is hidden from observation. Finally, we believe that similar systematic symmetry-based analyses could be used in the search for topological superconductors, Weyl semimetals, or other magnetoelectric and/or multiferroic classes of materials.

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