

Possible chiral spin-liquid phase in noncentrosymmetric $RBaCo_4O_7$ D. D. Khalyavin,¹ P. Manuel,¹ and L. C. Chapon²¹ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, United Kingdom²Institut Laue-Langevin, BP 156X, 38042 Grenoble, France

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Based on a symmetry approach, we propose a possible explanation of the weak ferromagnetic component recently observed in $YBaCo_3FeO_7$ [M. Valldor *et al.*, *Phys. Rev. B* **84**, 224426 (2011)] and other isostructural compounds in the high-temperature spin-liquid phase. Due to the polar nature of their crystal structure, a coupling between time-odd scalar spin chirality which we suggest as the primary order parameter and macroscopic magnetization is possible as follows from the general form of the appropriate free-energy invariant. The deduced pseudoproper coupling between both physical quantities provides a unique possibility to study the critical behavior of the chiral order parameter.

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The concept of symmetry and its spontaneous breaking at a phase transition is a central topic of condensed matter physics. Invariance of physical properties of crystals under spatial operations (such as rotations and reflections) and time reversal is the basis for their comprehensive description and classification. Time-reversal symmetry is the crucial ingredient to understand properties and describe phase transitions in magnetic systems with long-range spin-dipole ordering. A combination of this symmetry with the spatial operations form a powerful tool of magnetic symmetry based on which such fundamental phenomena as antisymmetric exchange¹ piezomagnetism² and the linear magnetoelectric effect³ have been predicted.

Besides conventional magnets exhibiting spontaneous breaking of time-reversal invariance at magnetic phase transitions, there is another type of systems where long-range spin ordering is suppressed by geometrical frustration. Usually, the geometrical frustration is caused by a combination of triangular-based exchange topology and antiferromagnetic interactions between neighbor spins. These systems fluctuate between degenerated ground states in the so-called “spin-liquid” phase, and can stay in this regime down to very low temperatures. The absence of long-range dipole magnetic ordering does not necessarily mean that spin-liquids keep time-reversal invariance. Some other spin quantities such as the toroidal moment ($\mathbf{T}$) and scalar spin chirality (χ) have been proposed as possible candidates for the time-reversal breaking order parameters as well.^{4–7} Despite considerable efforts to find systems with an actual realization of the spontaneous long-range toroidal or chiral order, in the absence of dipole ordering, only very recently a possible candidate for the latter has been found after observation of an anomalous Hall effect in the metallic pyrochlore $Pr_2Ir_2O_7$.^{8,9}

In insulating systems, however, identification of the long-range chiral ordering is more challenging but is not hopeless due to the possible coupling of the chiral order parameter to other measurable physical quantities. In this Rapid Communication, we discuss this possibility for the geometrically frustrated antiferromagnets $RBaMe_4O_7$ (R = rare earth or Y, Me = Co, Fe) with a polar hexagonal lattice. Based on a simple symmetry consideration, we show that the polar nature of the crystal structure allows an appropriate coupling of the

spin-chiral order parameter to spontaneous magnetization ($\mathbf{M}$) along the hexagonal axis. We propose this phenomenon as an explanation for the weak ferromagnetic component recently observed by Valldor *et al.*¹⁰ in the spin-liquid $YBaCo_3FeO_7$.

The prototype crystal structure of the $YBaCo_3FeO_7$ composition as in other members of the $RBaMe_4O_7$ family has hexagonal $P6_3mc$ symmetry¹¹ and consists of corner-sharing MeO_4 tetrahedra arranged in alternating kagome and triangular layers stacked along the c axis (Fig. 1).^{12,13} The Me sublattice forms a new exchange topology where geometrical frustration is inherent to the presence of both trigonal bipyramids and triangular clusters.^{14,15}

In spite of extremely strong exchange interactions in $YBaCo_3FeO_7$ (the paramagnetic Curie-Weiss temperature is ~ -2000 K), no long-range magnetic ordering has been observed down to 1 K.¹⁰ It should be pointed out that some of the $RBaCo_4O_7$ compounds exhibit spin ordering below ~ 100 K, which has been shown to be closely related to a strong magnetoelastic coupling, reducing the crystal structure symmetry down to monoclinic $P2_1$.¹⁶ Spin dynamics probed by high-resolution inelastic neutron scattering revealed a freezing below $T_f \sim 50$ K,¹⁰ thus in a wide temperature range above T_f , $YBaCo_3FeO_7$ is in a spin-liquid state. Surprisingly, a very weak ferromagnetic component ($\sim 10^{-3} \mu_B$ per Co/Fe ion) along the c axis and a hysteretic behavior of the magnetization in the magnetic field have been revealed below 590 K. The existence of small spontaneous magnetization in polycrystalline samples with the $YBa_{0.5}Ca_{0.5}Co_4O_7$ [below 387 K (Ref. 17)] and $YBaCo_4O_7$ [at room temperature (Ref. 18,19)] compositions had been reported before as well, indicating that this remarkable phenomenon is not a unique property of the Fe doped crystal. However, the higher transition temperature and the fact that the weak ferromagnetic component is observed in very clean single crystals and is anisotropic makes the $YBaCo_3FeO_7$ case a more compelling one. These observations, along with numerous neutron diffraction measurements proving the lack of a coherent magnetic Bragg scattering above 100 K,^{10,14,16,20,21} directly indicate that the time-reversal symmetry in the pure $RBaCo_4O_7$ or Fe doped compositions is broken without dipole spin ordering. The following fundamental question immediately arises: What breaks the time-reversal invariance in all these materials?

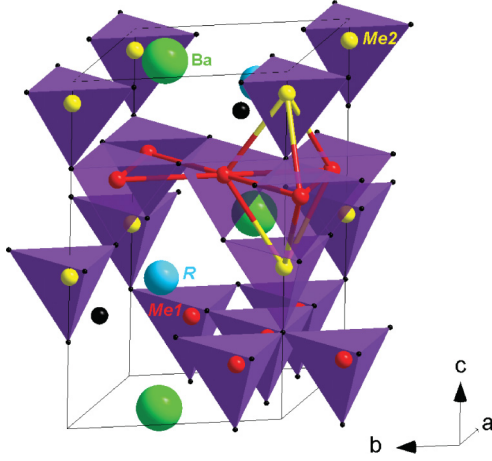


FIG. 1. (Color online) Schematic representation of the hexagonal $P6_3mc$ crystal structure of $RBaMe_4O_7$ as a corner-shared MeO_4 tetrahedral network. Metals ions in kagome and triangular layers are denoted as $Me1$ (red) and $Me2$ (yellow), respectively. Solid lines represent exchange bonds.

As was mentioned above, spin-dipole ordering is not the only order parameter which breaks time-reversal symmetry. Hypothetically, toroidal moment or scalar chirality is also considered as possible variants of the time-odd order parameters. The latter is a three-spin quantity defined as a mixed product of spins $\chi = \mathbf{S}_i \cdot [\mathbf{S}_j \times \mathbf{S}_k]$ in a triangular plaquette. The scalar chirality takes a nonzero value for noncoplanar spin states and its sign represents whether the noncoplanar structure is right or left handed. In spite of the time-odd nature of both $\mathbf{T}$ and χ order parameters, they have different transformational properties and therefore different types of coupling to macroscopic quantities. From a symmetry point of view, the spin chirality defined above is pseudoscalar, i.e., it changes sign at a mirror reflection and stays invariant under rotations, as is demonstrated in Fig. 2, where a result of reflection by the mirror planes and the threefold rotation of the $P6_3mc$ space group are shown. In group theoretical language, it means that the chiral order parameter transforms as the time-odd Γ_2^- irreducible representation of the $P6_3mc1'$ space group (see Table I—we use Miller and Love notation for the irreducible representations as implemented in the ISOTROPY program,²² where the superscript indicates parity with respect to time inversion). A ferromagnetic component along the sixfold axis (M_z) also transforms accordingly this representation and can therefore be linearly coupled to χ . Taking into account that magnetization is a vector and $\Gamma_2^- \otimes \Gamma_2^- \ni \Gamma_1^+$ and polarization along the c axis (P_z) transforms as Γ_1^+ , the general form of the free-energy invariant relating the macroscopic quantities can be written as $\chi \mathbf{M} \mathbf{P}$. Thus, in polar crystals, scalar chirality can be coupled to magnetization and, in a general case, where the polarization direction is not fixed by symmetry, a condensation of the chiral order parameter must induce magnetization in the direction of the polarization. In the case where polarization is frozen, as in $YBaCo_3FeO_7$ (or other members of the family), coupling between χ and $\mathbf{M}$ is pseudoproper and the critical behavior of both order parameters is identical. This offers the unique possibility to directly measure the critical exponent of

TABLE I. Matrix of irreducible representations (irreps) for generators of the $P6_3mc1'$ space group associated with wave vector $\mathbf{k} = 0$ and physical quantities that transform according to these representations. t is the time-reversal operator.

Irrep	$\{C_{6+} 00\frac{1}{2}\}$	$\{m_{xz} 00\frac{1}{2}\}$	t	Quantity
Γ_1^+	1	1	1	P_z
Γ_1^-	1	1	-1	T_z
Γ_2^-	1	-1	-1	M_z, χ
Γ_5^-	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	η_1, η_2
Γ_6^-	$\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	T_x, T_y

the chiral order parameter with sufficient accuracy to verify the universality class of these kinds of phase transitions.

In-plane (T_x, T_y) and out-of-plane (T_z) components of the macroscopic toroidal moment transform as the time-odd Γ_6^- and Γ_1^- representations, respectively (Table I), and cannot form an appropriate coupling invariant that is linear with respect to M_z .

The absence of both spatial and time inversions creates sufficient conditions for a linear magnetoelectric effect. The magnetic point group in the chiral phase of $RBaCo_4O_7$ is $6m'm'$ (the magnetic space group is $P6_3m'c'$), which allows $\alpha_{11} = \alpha_{22}$ and α_{33} components of the magnetoelectric tensor to be nonzero. Thus, measurement of the magnetization in the electric field or polarization in the magnetic field can be an additional probe of a long-range chiral order in insulating crystals.

The symmetry-based phenomenological consideration presented above is not able to reveal the microscopic origin of the phase transition to the chiral phase. However, let us discuss the symmetry aspects of the possible interactions favoring a noncoplanar spin arrangement in the case of well-defined local correlations. First, we note that antisymmetric Dzyaloshinskii-Moriya (DM) interactions can in some circumstances create conditions for a nonzero scalar chirality in a spin triangle, as shown in Fig. 3 (left). The phenomenological free-energy term responsible for these interactions is written in the form of $\mathbf{D}_{ij} \cdot [\mathbf{S}_i \times \mathbf{S}_j]$, where $\mathbf{D}_{ij}$ is the so-called Dzyaloshinskii vector whose direction depends on the crystal symmetry.²³ In particular, in the hexagonal lattice of $RBaCo_4O_7$, it must be parallel to the mirror planes bisecting the ij bonds and can be decomposed into two components: out-of-plane $\mathbf{D}_{out}$ (parallel to the c axis) and in-plane $\mathbf{D}_{in}$ (perpendicular to the c axis). Due to the polar nature of the structure, the out-of-plane component is always either up or down in the whole crystal. This component removes the degeneracy between the two planar spin configurations with a different vector chirality (defined as a vector product of the two neighboring spins, averaged over three spin pairs $\frac{2}{3\sqrt{3}} \sum_{(i,j)} [\mathbf{S}_i \times \mathbf{S}_j]$, where the summation is taken over three pairs of sites along the sides of the triangle in an anticlockwise direction) shown in Fig. 3(a). Then, the $\mathbf{D}_{in}$ component deviates the spins from the (ab) plane for the case when $\sum_{(i,j)} [\mathbf{S}_i \times \mathbf{S}_j] \uparrow \uparrow \mathbf{D}_{out}$ and leaves them coplanar when $\sum_{(i,j)} [\mathbf{S}_i \times \mathbf{S}_j] \uparrow \downarrow \mathbf{D}_{out}$. Thus, depending on the direction of $\mathbf{D}_{out}$, the antisymmetric DM term can select noncoplanar spin configurations.

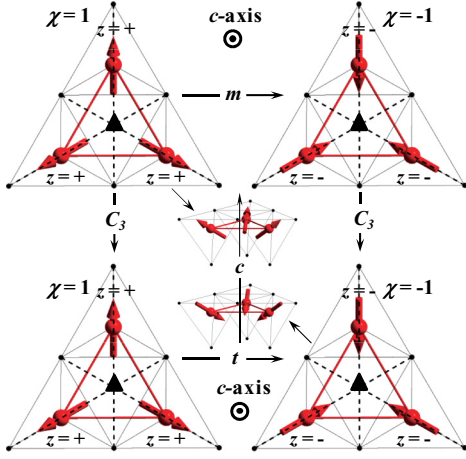


FIG. 2. (Color online) Transformational properties of three non-coplanar spins in a triangle (for simplicity, we arbitrarily took these spins to create equal angles between them but actually the angles can be different). The scalar chirality χ changes sign under the mirror reflection m and time inversion t but does not change it under the rotation C_3 . Intersections of the mirror planes of the triangle with the plane containing it are shown as dotted lines. The signs of the z component for each spin are shown as + or -.

The case when $\mathbf{D}_{in}$ does not couple a z component to the spins in a triangle [Fig. 3(b), right] is of particular interest. It is easy to see that an admixture of the out-of-plane spin component does not change the m' symmetry of the planar spin configuration and therefore can be added to it [Fig. 3(c), right]. The coupling, however, cannot be linear since the z component is invariant with respect to the threefold axis, while the planar spin configuration is not. So the out-of-plane component has the higher symmetry ($3m'$) and can be coupled only as a linear-cubic term between the associated order parameters due to the necessary invariance with respect to the time inversion. Thus, interactions which relate the in-plane and out-of-plane spin components in this case are distinct from DM term coupling orthogonal components with identical transformational properties (bilinear coupling).

More generally, the global distortions of the type shown in Fig. 3(a) (right) keeping the translational invariance of the crystal can be presented as combinations of basis functions of the Γ_5^- irreducible representation of the $P6_3mc1'$ space group (Table II). The associated two-dimensional order parameter (η_1, η_2) forms a general coupling invariant with the out-of-plane ferromagnetic component, $3M_z\eta_1^2\eta_2 - M_z\eta_2^3$, which is reduced down to the simple linear-cubic term $M_z\eta_2^3$ for the $(0, \eta_2)$ direction. The latter is the equilibrium order parameter for the most symmetric variant of the spin structure with the vector chirality shown in Fig. 3(a) (right). Minimization of the free-energy part, $F = \gamma M_z^2 + \beta M_z\eta_2^3$, with respect to M_z , gives a nonzero equilibrium value for the latter, $M_z = -\frac{\beta\eta_2^3}{2\gamma}$. Thus, in spite of the passive role of the DM interactions, the macroscopic magnetization and scalar chirality are expected to be nonzero due to the existence of the linear-cubic type of coupling. The chiral free-energy term $\chi \mathbf{M} \mathbf{P}$ (which shows that the system gains energy in the case of the noncoplanar spin arrangement) can clearly provide this coupling with some “adopted” to local symmetry meaning of the $\mathbf{M}$ and

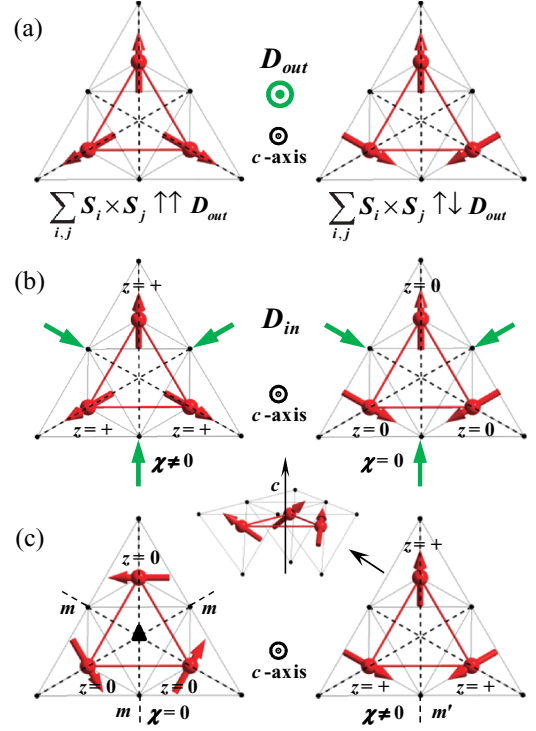


FIG. 3. (Color online) Two variants of coplanar spin configurations in a triangle with parallel ($\uparrow\uparrow$) and antiparallel ($\uparrow\downarrow$) directions of the vector chirality and $\mathbf{D}_{out}$ component. The latter was arbitrarily chosen to be in the up direction (a). Impact of the in-plane $\mathbf{D}_{in}$ component on these spin configurations (b). Spin configuration forbidding (left) and allowing (right) the z component and scalar chirality to be nonzero (c).

$\mathbf{P}$ quantities, and in a general case it represents antisymmetric interactions that are distinct from DM. These interactions imply a “chiral dependent” part of the exchange Hamiltonian, tending to bring three spins to the mutually orthogonal orientation. The local meaning of $\mathbf{M}$ and $\mathbf{P}$ adopted for a single triangular unit in a structure should ensure vanishing of the coupling invariant for some spin configurations whose symmetry forbids noncoplanar states as in the case of the $3m$ point group shown in Fig. 3(c) (left). In some particular cases, the DM exchange can contribute to the free-energy chiral term, too (as was shown above), since the existence of the bilinear coupling invariant between order parameters means

TABLE II. Symmetrized combinations of the atomic spins S on the Wyckoff position 6c (kagome layer) transforming as components of the two-dimensional Γ_5^- order parameter η_i ($i = 1, 2$) (Ref. 22).

η_i	S	1 ^a	2	3	4	5	6
η_1	S^x	1	-1	0	0	-1	1
	S^y	0	-1	1	-1	0	1
	S^z	0	0	0	0	0	0
η_2	S^x	$-\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	$-\frac{2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$
	S^y	$-\frac{2}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$
	S^z	0	0	0	0	0	0

^a 1: $(x, -x, z)$; 2: $(x, 2x, z)$; 3: $(-2x, -x, z)$; 4: $(2x, x, z + \frac{1}{2})$; 5: $(-x, x, z + \frac{1}{2})$; 6: $(-x, -2x, z + \frac{1}{2})$; $x \sim \frac{1}{6}$; $z \sim \frac{11}{16}$.

the existence of a linear-cubic one as well. To further clarify the relevant interactions responsible for the chiral state in $R\text{BaMe}_4\text{O}_7$, numerical simulations based on the Monte Carlo algorithm with different terms in the magnetic Hamiltonian including the chiral-dependent $\chi\mathbf{MP}$ one are desirable.

In conclusion, based on a symmetry consideration, we argue that the weak ferromagnetic component, measured in $\text{YBaCo}_3\text{FeO}_7$ and some other isostructural compositions, in a spin-liquid regime, is related to long-range chiral ordering. The coupling between both macroscopic physical quantities is possible in polar crystals due to a phenomenological trilinear

invariant of the form $\chi\mathbf{MP}$. This invariant, in a general case, represents interactions distinct from Dzyaloshinskii-Moriya ones and provides a linear-cubic coupling between orthogonal spin components. Due to the frozen nature of the polarization in the hexagonal lattice of $R\text{BaCo}_4\text{O}_7$, the coupling between χ and $\mathbf{M}$ is pseudoproper and the critical behavior of both order parameters is identical. This offers a unique possibility to identify the universality class of these exotic phase transitions. The result obtained here provides a physical ground for a search of other possible systems where spin chirality is the primary order parameter.

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