Chiral spin pairing in helical magnets

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A concept of chiral spin pairing is introduced to describe a vector-chiral liquid-crystal order in frustrated spin systems. It is found that the chiral spin pairing is induced by the coupling to phonons through the Dzyaloshinskii-Moriya interaction and the four-spin exchange interaction of the Coulomb origin under the edge-sharing network of magnetic and ligand ions. This produces two successive second-order phase transitions upon cooling: an O(2) chiral spin nematic, i.e., spin cholesteric, order appears with an either parity, and then the O(2) symmetry is broken to yield a helical magnetic order. Possible candidate materials are also discussed as new multiferroic systems.

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The chirality in the electronic spin texture introduced by a geometrical frustration and/or the relativistic spin-orbit interaction has been one of the key concepts in strongly correlated electron systems. The scalar spin chirality $\mathbf{a}$, i.e., the scalar triple product of three non-coplanar spins, is odd under the time-reversal $(T)$ and even under the space-inversion $(I)$, and gives rise to a large anomalous Hall effect [4, 5, 6, 7, 8]. On the other hand, central to this Letter is the vector spin chirality [9], i.e., the vector product of two noncollinear spins. It is $T$-even and $I$-odd, and can produce the ferroelectric polarization in Mott insulators through the spin-orbit interaction [10, 11, 12, 13, 14, 15, 16, 17], even for spin-1/2 systems [17, 18, 19].

The vector-chiral spin order is realized in conventional helical magnets. In principle, it is even possible that the chiral or parity symmetry is broken but the time-reversal symmetry is not. This state having finite spin correlation lengths is categorized into a liquid or a liquid crystal of spins, which is of our main interest, while the magnetically ordered state into a solid. The issue of the chiral spins, which is of our main interest, while the magnetically ordered state into a solid. The issue of the chiral spins, which is of our main interest, while the magnetically ordered state into a solid. The issue of the chiral spins, which is of our main interest, while the magnetically ordered state into a solid. The issue of the chiral spins, which is of our main interest, while the magnetically ordered state into a solid.
coefficients to those terms become unity. Quadratic interaction terms with the coupling constants \( u = u_0 > 0 \) and \( v = v_0 = -u_0/3 \) can be obtained by softening the constraint that amplitudes of spins must be fixed, \( \bar{S}(r)^2 \approx S^2 \), and substituting Eq. (1) into the quartic term \( \frac{1}{2} f dr (\bar{S}_r)^2 \). Then, the Hamiltonian given by Eq. (2) is isomorphic to a classical O(3) \times O(2) nonlinear-\( \sigma \) model \[27\]. Now helical and collinear magnetic orders are expressed by \( \langle \vec{a} \rangle \times \langle \vec{b} \rangle \neq 0 \) and \( \langle \vec{a} \rangle \times \langle \vec{b} \rangle = 0 \), respectively. The vector-chiral order is characterized by \( \langle \vec{a} \times \vec{b} \rangle \neq 0 \). \( u \) and \( v \) are modified from the Heisenberg values by additional interactions as shown later.

\[
\begin{align*}
\text{FIG. 1: } \text{(Color online) Phase diagram of the Ginzburg-Landau Hamiltonian given by Eq. (2) and the ordering patterns. Note that } \bar{\mu}_s = -\mu_s. \text{ For details, see the text.}
\end{align*}
\]

To derive this result, we have employed the mode coupling approximation, where the average value and the optimal Gaussian fluctuation form of the order parameters are determined by the variational principle \[34\]. First, we decompose the fields into the condensed and normal components as \( \langle \bar{a}_q, \bar{b}_q \rangle = \delta a_q (A, B) + \langle \delta a_q, \delta b_q \rangle, \langle \bar{a}_r \rangle = \bar{A} \) and \( \langle \bar{b}_r \rangle = \bar{B} \) give the ordered magnetic moment through Eq. (1), \( \bar{A}, \bar{B} \) is subject to the stationary condition of the free energy with respect to \( \langle \delta a, \delta b \rangle \). To treat the Gaussian fluctuations around the saddle point, we consider the variational quadratic Hamiltonian \( \mathcal{H}_{\text{var}} = (a_0/2\pi)^{-3} \int d\mathbf{q} \sum_{i,j=1}^3 (\delta a_{iq}, \delta b_{iq}) G_{ij}^{-1} (\delta a_{jq}, \delta b_{jq}) \) with the \( 6 \times 6 \)-matrix Green’s function \( G_Q \) defined by

\[
\dot{G}_Q^{-1} = (\delta_{ij} q^2 + \mu^{ij}) \bar{\rho}^i \bar{\rho}^j + \delta \mu^{ij} \bar{\rho}^i \bar{\rho}^j + \Delta^i_{ij} \bar{\rho}^i + \Delta^j_{ij} \bar{\rho}^j (3)
\]

with the \( 2 \times 2 \) identity matrix \( \bar{\rho}^i \) and the Pauli matrices \( (\bar{\rho}^x, \bar{\rho}^y, \bar{\rho}^z) \) operating on the \((a, b)\) space. Here, the variational parameters \( \mu^{ij} \), \( \delta \mu^{ij} \), \( \Delta^i_{ij} \), and \( \Delta^j_{ij} \) are determined from the self-consistent equations,

\[
\begin{align*}
\mu^{ij} &= \delta^{ij} \left[ \mu + (u + v) \sum_{\ell} \left( A^{\ell 2} + B^{\ell 2} + \gamma_0^{\ell \ell} \right) \right] + (u - v) \left( A^{\ell} A^\ell + B^{\ell} B^\ell + \gamma_0^{\ell \ell} \right), \\
\delta \mu^{ij} &= -v \delta^{ij} \sum_{\ell} \left( A^{\ell 2} - B^{\ell 2} + \gamma_0^{\ell \ell} \right) + (u + v) \left( A^{\ell} A^\ell - B^{\ell} B^\ell + \gamma_0^{\ell \ell} \right), \\
\Delta^{ij}_s &= -v \delta_{ij} \sum_{\ell} \left( 2 A^{\ell} B^\ell + \gamma_0^{\ell \ell} \right) + (u + v) \left( A^{\ell} B^\ell + A^\ell B^{\ell} + \gamma_0^{\ell \ell} \right), \\
\Delta^{ij}_a &= (u + 3v) \left( A^{\ell} B^\ell - A^\ell B^{\ell} + v \gamma_0^{\ell \ell} \right),
\end{align*}
\]

where \( \gamma_0^{ij} \equiv \langle \delta a_0^i, \delta a_0^j \rangle, \gamma_0^{ij} \equiv \langle \delta b_0^i, \delta b_0^j \rangle, \gamma_0^{ij} \equiv \langle \delta a_0^i, \delta b_0^j \rangle, \gamma_0^{ij} \equiv \langle \delta b_0^i, \delta a_0^j \rangle, \) and \( \gamma_0^{ij} \equiv \langle \delta b_0^i, \delta b_0^j \rangle \) are calculated from

\[
\gamma^{ij}_0 = a_0^3 \int \frac{d q}{(2\pi)^3} \text{Tr} \hat{G}_q^{ij} \rho^r, \tag{5}
\]

where the trace \( \text{Tr} \) is taken only in the \((a, b)\) space.

We start from the disordered phase where all the variational parameters including \( \bar{A}, \bar{B} \) vanish except the mass \( \mu^r \equiv \mu^{rr} \). Then, the self-consistent equations \[41\] can be linearized with respect to the dimensionless variational order parameters \( \bar{\mu}^{ij} \equiv \mu^{ij}/A^2 \) \((i \neq j)\), \( \bar{\mu}^{ij} \equiv \mu^{ij}/A^2 \), \( \bar{\Delta}^{ij}_s \equiv \Delta^{ij}_s/A^2 \), and \( \bar{\Delta}^{ij}_a \equiv \Delta^{ij}_a/A^2 \),

\[
\begin{align*}
\bar{\mu}^r &= \mu^r / A^2 = \bar{\mu} + 4(\bar{a} + \bar{\nu}) g(\bar{\mu}^r), \\
\bar{\mu}^{ij} &= -2(\bar{a} - \bar{\nu}) g(\bar{\mu}^{ij}) \text{ for } i \neq j, \\
\left( \begin{array}{c}
\delta \mu^{ij} \\
\Delta^{ij}_s \\
\Delta^{ij}_a
\end{array} \right) &= -2 \left( \begin{array}{c}
\delta \mu^{ij} \\
\Delta^{ij}_s \\
\Delta^{ij}_a
\end{array} \right) \left[ -3 \delta_{ij} (\bar{a} + \bar{\nu}) \right] f(\bar{\mu}^r), \\
\bar{\Delta}^{ij}_s &= -2 \Delta^{ij}_s (\bar{a} + 3 \bar{\nu}) f(\bar{\mu}^r),
\end{align*}
\]

with

\[
\begin{align*}
g(\bar{\mu}^r) &= 1 - \sqrt{\bar{\mu}^r} \arctan \frac{1}{\sqrt{\bar{\mu}^r}}, \\
f(\bar{\mu}^r) &= \frac{1}{2} \left( \arctan \frac{1}{\sqrt{\bar{\mu}^r}} - \frac{1}{1 + \bar{\mu}^r} \right). \tag{7a, b}
\end{align*}
\]

If we ignore the spin pairing, i.e., \( \delta \mu^{ij} = \Delta^{ij}_s = \Delta^{ij}_a = 0 \), Eq. (6a) always gives a direct phase transition from the paramagnet to a helical (collinear) magnet for \( v < 0 \) at a critical point \( \bar{\mu}^r = 0 \). However, a serious consideration on the spin pairs \( \delta \mu^{ij}, \Delta^{ij}_s, \) and \( \Delta^{ij}_a \) reveals that a spin liquid-crystal phase emerges before the magnetic orders set in. Note that \( g(\bar{\mu}^r) \) and \( f(\bar{\mu}^r) \) are positive and that \( f(\bar{\mu}^r) \) diverges as \( \pi/(4 \sqrt{\bar{\mu}^r}) \) for \( \bar{\mu}^r \to 0 \). Then, as far as the Hamiltonian is stable, i.e., \( u + v > 0 \), there appear two possibilities for spin paired states. (i) When
the interaction for the antisymmetric spin pairing channel is attractive, namely, $v/u = \tilde{v}/\tilde{u} < -1/3$ in Eq. (6c), then it forms the chiral spin pairs $\Delta R^a \neq 0$ through a second-order phase transition. The critical value of $\mu^c$ is determined by $f(\mu^c) = -1/(2(\tilde{u} + 3\tilde{v}))$ from Eq. (6d) with $\mu^c > 0$: the magnetic long-range order is absent. This represents a O(2)-symmetric chiral spin nematic [29] or spin cholesteric. (ii) When $\sqrt{u}/\tilde{u} > 1/2$ in Eq. (6c), the symmetric spin pairs are formed, $(\delta\mu^c, \Delta R^a) \neq 0$. However, this condition is usually difficult to be realized starting from the Heisenberg point $v/u = -1/3$. In the following, we concentrate on the case of (i) $v/u < -1/3$, which is more likely to occur.

In the spin cholesteric phase characterized by $\Delta R^a \propto \epsilon_{ijz}$ with the fully antisymmetric tensor $\epsilon_{ijz}$, the Green’s function can be described by

$$\tilde{C}_{q}^{ij} = \frac{1}{2} \sum_{\sigma \pm} \frac{\delta_{ij} - i\sigma\epsilon_{ijz}\hat{\mu}^y}{\mu^y + q^2 - \sigma(1 - \delta_{iz})\Delta_a},$$

(8)

Here, $\mu_{\|} \equiv \mu^{xx} = \mu^{yy}$, $\mu_{\perp} \equiv \mu^{zz}$, and $\Delta_a$ are determined by the numerical solution to the self-consistent equations,

$$\hat{\mu}_{\|} \equiv \mu_{\|} + 2\hat{u}h^+ (\hat{\mu}_{\|}, 0) + (\tilde{u} + \tilde{v})h^+ (\hat{\mu}_{\|}, \Delta_a),$$

(9a)

$$\hat{\mu}_{\|} \equiv \mu_{\|} + (\tilde{u} + \tilde{v})h^+ (\hat{\mu}_{\|}, 0) + (3\tilde{u} + 3\tilde{v})h^+ (\hat{\mu}_{\|}, \Delta_a),$$

(9b)

$$\Delta_a \equiv - (\tilde{u} + 3\tilde{v})h^- (\hat{\mu}_{\|}, \Delta_a),$$

(9c)

which are derived from Eqs. (13) and (14), where $h^\pm (\hat{\mu}_{\|}, \Delta_a) = g(\hat{\mu}_{\|} - \Delta_a) \pm g(\hat{\mu}_{\|} + \Delta_a)$. Since $\mu_{\|} < \mu_{\perp}$ holds generally, the spins that are originally O(3)-symmetric now obtain the easy-plane XY anisotropy. Accordingly, the spin correlation has three nonvanishing branches:

$$\langle S^x_{r'v} S^x_{rv} \rangle = \chi_{r,r'} (\mu_{\|}) \cos Q \cdot (r - r'),$$

(10)

$$\langle S^y_{r'v} S^y_{rv} \rangle = \frac{1}{2} \sum_{\sigma = \pm} \chi_{r,r'} (\xi_{\|}^{-2}) \cos Q \cdot (r - r'),$$

(11)

with $i = x, y$ and the chiral spin correlation

$$\langle S^z_{r'v} S^z_{rv} \rangle = \sum_{\sigma = \pm} \chi_{r,r'} (\xi_{\|}^{-2}) \sin Q \cdot (r - r'),$$

(12)

where $\xi_{\|} \equiv 1/\sqrt{\mu_{||} - \sigma\Delta_a}$ and

$$\chi_{r,r'} (\xi^{-2}) \sim \frac{\alpha^2 \Lambda}{4\pi^2 \Lambda} \frac{\pi}{|r - r'|} \exp (-|r - r'|)$$

(13)

for a long-distance decay. These spin correlations are all short-ranged with two correlation lengths $\sim \xi_{\perp}$. The sign of the chirality $\Delta_a$ can be determined from that of $\langle S^x_{r'v} S^y_{rv} - S^y_{r'v} S^x_{rv} \rangle$. Further decreasing $\mu_{\|}$ becomes equal to $\Delta_a$, leading to a divergence of either $\xi_{\|}$ or $\xi_{\perp}$ and thus the second-order phase transition to the helical magnet. Note that all the above structures should appear in the static spin correlations, which can be directly studied by the polarization dependence of the incident and/or scattered neutrons [33].

In fact, the coupling constants $u$ and $v$ are modified by (i) the coupling of spins to longitudinal phonons with the wavevector $\pm 2Q$ through the magnetostriction, (ii) that to transverse phonons with the wavevector $0$ through the DM interaction, and (iii) the four-spin ring-exchange interactions, i.e., $u = u_0 + \delta u_{\text{DS}} + \delta u_{\text{DM}} + \delta u_{\text{ring}}$ and $v = -v_0/3 + \delta v_{\text{DM}} + \delta v_{\text{ring}}$.

(i) The magnetostriction arises from

$$- \delta J \sum_{r,r'} \langle \tilde{X}_{r'} - \tilde{X}_r \rangle \cdot \tilde{e}_{r'} \cdot \tilde{e}_r \cdot \tilde{S}_r \cdot \tilde{S}_{r'} + \sum_r \left[ \frac{\tilde{B}^2}{2M} + \frac{1}{2} \tilde{K} \tilde{X}_r^2 \right]$$

(14)

with the spatial derivative $\delta J$ of the exchange interaction, the unit vector $\tilde{e}_{r'}$ and $\tilde{e}_r$ pointing from $r$ to $r'$, the mass $M$ of the magnetic ion, the spring constant $K$ associated with its shift $\tilde{X}_r$, and the conjugate momentum $\tilde{P}_r$. Substituting Eq. (11) into Eq. (14) and integrating over $\tilde{X}_r$, we obtain $\delta u_{\text{DM}} = \delta u_{\text{DS}} = (c^{-1} \delta J \sin Q \cdot \delta)^2 / 2K$ where $c$ is the average spin-wave velocity.

(ii) Additional terms to the Hamiltonian reads

$$\frac{1}{2} \sum_{r,r'} \left[ - \delta D \cdot \tilde{S}_r \cdot \tilde{S}_{r'} + \frac{\delta D^2}{2m_{\text{L}}} \right]$$

(15)

Here, $\delta D = \lambda \tilde{X}_r \cdot \tilde{S}_r$ represents the antisymmetric DM coupling vector between the nearest-neighbor spin pair $\tilde{S}_r$ and $\tilde{S}_r$ located at the discrete lattice sites $r$ and $r'$, respectively, with the coupling constant $\lambda$ and a transverse shift $\tilde{X}_r$ of the ligand ion [27]. For simplicity, we have assumed that the ligand ion is located at the center of nearest-neighbor bonds of spins. Because of this coupling, the chiral order $\langle \tilde{S} \cdot \tilde{b} \rangle \neq 0$ simultaneously produces both macroscopic averages of $\tilde{x}$ and the electric polarization in proportion to $\langle \tilde{a} \cdot \tilde{b} \rangle$ and $Q \times \langle \tilde{a} \times \tilde{b} \rangle$, respectively. Note that applied electric field plays the same role as the average value of $\tilde{x}$. Substituting Eq. (11) into Eq. (15) and integrating over $\tilde{x}_r$, we obtain $\delta u_{\text{ring}} = 0$ and $\delta u_{\text{DS}} = - (c^{-1} \delta J \sin Q \cdot \delta)^2 / 2K$ with the nearest-neighbor coordination vector $\delta$.

(iii) In the case of corner-sharing network of magnetic and ligand ions, four-spin ring-exchange interaction arises from the strong-coupling expansion. Substituting Eq. (11) into the ring-exchange Hamiltonian around four sites $r_i$ ($i = 1, \ldots, 4$) in a $xy$-plane plaquette,

$$J_{\text{ring}} (P_{r_1 r_2 r_3 r_4} + P_{r_2 r_3 r_4 r_1} - P_{r_1 r_3 r_2 r_4} - P_{r_1 r_3 r_4 r_2})$$

(16)

with $P_{r_1 r_2' r_3' r_4'} \equiv \langle \tilde{S}_{r'} \cdot \tilde{S}_{r''} \rangle (\tilde{S}_{r'} \cdot \tilde{S}_{r''})$ for spin-1/2 [32]. 33, we obtain $\delta u_{\text{ring}} = c^{-4} J_{\text{ring}} (\cos^2 Q_x + \cos^2 Q_y - 1/2)$ and $\delta u_{\text{DS}} = c^{-4} J_{\text{ring}} (\sin^2 Q_x + \sin^2 Q_y - 1/2)$.

On the other hand, in the case of edge-sharing network, the above ring-exchange is suppressed, while the second-order strong-coupling perturbation of the four-site Coulomb interaction in the unit square gives a still finite contribution of the form

$$- K_{1} [P_{r_1 r_2 r_3 r_4} + P_{r_2 r_3 r_4 r_1} - K_{2} P_{r_1 r_3 r_2 r_4}$$

(17)
where \( K_1 \sim 4I_{2134}^2/U \), \( K_2 \sim 4(I_{2134} - I_{1234})^2/U < K_1 \), and 
\[ I_{ijkl} = \int d\rho d\rho' e^{e^2/|\rho - \rho'|} \phi(\rho - r_i)\phi(\rho' - r_j)\phi(\rho' - r_k)|\phi(\rho - r_l) \]
with the local Coulomb repulsion \( U \) and the Wannier function \( \phi(\rho) \) centered at the magnetic ion site. Again substituting Eq. (4) into Eq. (17), we obtain 
\[ \delta v^{\text{ring}} = -c^{-4}(2K_1 + K_2)(\cos^2 Q_x + \cos^2 Q_y - \frac{1}{2}) \quad \text{and} \quad \delta v^{\text{ind}} = c^{-4}K_1(\cos^2 Q_x + \cos^2 Q_y - \frac{1}{2}) + K_2/2. \]

Putting the above considerations together, the deviation of the parameter \( v/u \) from the Heisenberg value \(-1/3\), which plays a crucial role in determining the phase diagram, is eventually given by

\[ v/u + \frac{1}{3} \sim \sum_{\delta} \frac{\sin^2 Q \cdot \delta}{3c^4 u_0} \left[ \frac{\lambda^2}{2K} - \frac{3\lambda^2}{2\kappa} + 4J^{\text{ring}} - (K_1 - K_2) \right]. \]

Namely, the DM interaction and the Coulombic four-spin ring-exchange yield a negative shift of \( u/v \) and favor the chiral spin pairing, whereas the magnetostriction and the kinetic four-spin ring-exchange interaction do not.

Let us discuss a possibility of observing the spin cholesteric phase in real systems. First, the easy-axis single spin anisotropy is unfavorable, since it produces a mass between the two fields to be paired and suppresses the pairing. On the other hand, the chiral order remains in the easy-plane anisotropy since the chiral order parameter is now a scalar which forms a long-range order more easily than the \( O(3) \) vector. In the case of \( R\text{MnO}_3 \) (\( R=\text{Tb, Dy} \)) [10], the spin of the Mn ions is \( S = 2 \) and the single spin anisotropy plays a dominant role for the successive phase transitions from paramagnet to incommensurate collinear states and to incommensurate helical state as the temperature is lowered. Especially the transition to the helical state is of first-order, and hence the magnetic ordering temperature.

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