Nonrelativistic Multiferroicity in the Nonstoichiometric Spin s=1/2 Spiral Chain Cuprate LiCu$_2$O$_2$

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We argue for a recently observed puzzling multiferroic behavior in s=1/2 1D chain cuprate LiCu$_2$O$_2$ with edge-shared arrangement of CuO$_4$ plaquettes and incommensurate spiral spin ordering which is obviously counterintuitive within the framework of spiral magnetic ferroelectricity.

Recent observations of multiferroic behaviour concomitant the incommensurate spin spiral ordering in chain cuprates LiCuVO$_4$\textsuperscript{1,2,3} and LiCu$_2$O$_2$\textsuperscript{4,5} challenge the multiferroic community. At first sight, these cuprates seem to be prototypical examples of 1D spiral-magnetic ferroelectricity revealing the relativistic mechanism of "ferroelectricity caused by spin-currents"\textsuperscript{6} with the textbook expression for the uniform polarization induced by a spin spiral with the wave vector $\mathbf{Q}$: $\mathbf{P} \propto [\mathbf{e}_3 \times \mathbf{Q}]$, where $\mathbf{e}_3$ is a vector orthogonal to the spin spiral plane or $\mathbf{P}_{ij} \propto [\mathbf{R}_{ij} \times [\mathbf{S}_i \times \mathbf{S}_j]]$, where $\mathbf{R}_{ij}$ denotes the vector connecting the two sites and $[\mathbf{S}_i \times \mathbf{S}_j]$ is a local spin current. However, the both systems reveal a mysterious behavior with conflicting results obtained by different groups. Indeed, Yasui \textit{et al.}\textsuperscript{2} claim the LiCuVO$_4$ reveals clear deviations from the predictions of spin-current model\textsuperscript{6} while Schrettle \textit{et al.}\textsuperscript{7} assure of its applicability. In contrast to LiCuVO$_4$, the LiCu$_2$O$_2$ shows up a behavior which is obviously counterintuitive within the framework of spiral-magnetic ferroelectricity. It is worth noting that at variance with Park \textit{et al.}\textsuperscript{4}, Naito \textit{et al.}\textsuperscript{3} have not found any evidence for ferroelectric anomalies in LiCu$_2$O$_2$. Such a discrepancy one observes in microscopic model approaches as well. The relativistic LSDA calculations\textsuperscript{8} seemingly explain the LiCuVO$_4$ data but fail in case of LiCu$_2$O$_2$. However, a detailed analysis of relativistic effects for the system of $e_g$-holes in a perfect chain structure of edge-shared CuO$_4$ plaquettes as in LiCuVO$_4$ and LiCu$_2$O$_2$ shows that the in-chain spin current does not produce an electric polarization because of an exact cancellation of two Cu-O-Cu paths. Moreover, recently we have shown\textsuperscript{9} that the multiferroicity in LiCuVO$_4$ may have nothing to do with relativistic effects and can be consistently explained, if the nonrelativistic exchange-induced electric polarization on the out-of-chain Cu$^{2+}$ centers substituting for Li-ions in LiVCuO$_4$ is taken into account. Below we argue that a similar mechanism which takes into account the exchange-induced electric polarization on the Cu$^{2+}$ centers, substituting unexpectedly for Cu$^{1+}$-ions, is at work in LiCu$_2$O$_2$.

LiCu$_2$O$_2$ is orthorhombic mixed-valent compound with copper ions in the Cu$^{3+}$ and Cu$^{1+}$ valence states.\textsuperscript{10} The unit cell contains four magnetic Cu ions belonging to two pairs of CuO$_2$ chains formed by edge-shared Cu$^{2+}$O$_4$ plaquettes running along the crystallographic b-axis and linked by the LiO$_5$ double chains. Alternating double parallel chains, containing either Li or Cu atoms, form the sheets which are interconnected by Cu$^{1+}$ in O-Cu-O dumbbells.

The first experimental evidence of magnetic incommensurability in LiCu$_2$O$_2$ was obtained independently by Gippius \textit{et al.}\textsuperscript{11} and Masuda \textit{et al.}\textsuperscript{12} from $^{6,7}$Li NMR and neutron diffraction measurements, respectively. Any spins related by a translation along the c axis and a axis are parallel and antiparallel to each other, respectively. A good fit to neutron diffraction data was obtained with all spins confined to the ab crystallographic plane, thus forming ab-plane spin spirals running along b axis: $\mathbf{S}(y) = S(\cos \theta, \sin \theta, 0)$, where $\theta = q y + \alpha$, $\alpha$ is a phase shift. Park \textit{et al.}\textsuperscript{4} have found that the incommensurate spin ordering in LiCu$_2$O$_2$ below $T_N \approx 23$ K is accompanied by a ferroelectric transition with a puzzling anisotropy and field dependence which are reproduced schematically in Fig. 1. First of all, the electric polarization in zero field is directed along the c axis implying in accordance with the concept of spin current induced ferroelectricity that the spiral spins lie in the bc-plane in sharp contrast with earlier neutron diffraction data.\textsuperscript{12} When a magnetic field applied along the b axis (see Ref.\textsuperscript{4} for the making use of a, b notations in ab-twinned crystal), $P_c$ decreases and $P_a$ increases, im-

![FIG. 1: Direction of ferroelectric polarization in LiCu$_2$O$_2$ for different spin spiral plane orientation.](image-url)
in the CuO$_2$ chains, dimer-type effects as in other hole doped chains would be observed experimentally. Also the spiral state observed in the neutron diffraction would be strongly disturbed by the presence of these holes. What is the ground state of the single hole configuration of Cu$^{2+}$ ion in the native Cu$^{1+}$ interchain sites? Purely electrostatic arguments made within the framework of the point charge model, supported by account for Cu 3d-O 2p covalency, point to a competition of $d_{xz}$ and $d_{yz}$ orbitals while strong intra-atomic s-$d_{xz}$ hybridization singles out the $d_{yz}$ orbital to be a main candidate for the ground state. The Cu$^{2+}$ substituents in native Cu$^{1+}$ positions form strongly polarizable entities which electric polarization due to a parity-breaking exchange interaction with Cu$^{2+}$ spin spirals explains all the puzzles observed by Park et al. This unconventional exchange coupling can be easily illustrated for, e.g., the one-particle (electron/hole) center in a crystallographically centrosymmetric position of a magnetic crystal when all the particle states can be of definite spatial parity, even (g) or odd (u), respectively. Having in mind the 3d centers we’ll assume an even-parity ground state $|g\rangle$. For simplicity we restrict ourselves by only one excited odd-parity state $|u\rangle$. The exchange coupling with the surrounding spins can be written as follows:

$$
\hat{V}_{ex} = \sum_n \hat{I}(\mathbf{R}_n)(\mathbf{s} \cdot \mathbf{S}_n),
$$

where \(\hat{I}(\mathbf{R}_n)\) is an orbital operator with a matrix

$$
\hat{I}(\mathbf{R}_n) = \begin{pmatrix}
I_{gg}(\mathbf{R}_n) & I_{gu}(\mathbf{R}_n) \\
I_{ug}(\mathbf{R}_n) & I_{uu}(\mathbf{R}_n)
\end{pmatrix}.
$$

The parity-breaking off-diagonal part of the exchange coupling can lift the center of symmetry and mix $|g\rangle$ and $|u\rangle$ states giving rise to a nonzero electric dipole polarization of the ground state

$$
\mathbf{P} = 2c_{gu}\langle g|\mathbf{e}r|u\rangle = \sum_n \Pi_n(\mathbf{s} \cdot \mathbf{S}_n)
$$

with

$$
\Pi_n = 2I_{gu}(\mathbf{R}_n)(\langle g|\mathbf{e}r|u\rangle)/\Delta_{ug} (\Delta_{ug} = \epsilon_u - \epsilon_g).
$$

Strictly speaking, the parity-breaking exchange coupling of native Cu$^{2+}$ center in CuO$_2$ chain (hole ground state $|g\rangle \propto d_{xy}$) with neighbouring Cu$^{2+}$ substituent (hole ground state $|g\rangle \propto d_{yz}$) will result in the $ab$-plane electric polarization of Cu$_4$ chain plaquettes and the $c$-axis polarization of the Cu$^{2+}$ substituent.

Unit cell of LiCu$_2$O$_2$ contains two types (left and right) of native Cu$^{1+}$-positions (see Fig.1) with four neighbouring Cu$^{2+}$ centers in the two CuO$_2$ chains. Within the framework of our model the both "left" A-type and "right" B-type substituent centers differ by the spin spiral phase shift $\alpha = \pi/2$ and $\alpha = -\pi/2$ with respect to the lower chain, and by orientation of the generated electric dipole moments: $d_a(A) = -d_a(B) = d/\sqrt{2}$, $d_b(A) = d_b(B) = d/\sqrt{2}$, $d_c(A) = d_c(B) = d_c$. Here we ignore the weak influence of the adjacent chain in the third

FIG. 2: An idealized view of crystal structure of LiCu$_2$O$_2$(upper bilayer). A "left" site impurity center with Cu$^{2+}$-ion substituted for Cu$^{1+}$-ion is inbetween upper and lower CuO$_2$ chains from the same unit cell. Shown is the hole density distribution in $d_{xz}$ orbital. The exchange induced dipole moments are shown by arrows.
CuO chain belonging to the adjacent bilayer. According to LDA calculation there is practically no hybridization with that chain.\(^\text{11}\)

To describe different configurations of the spin neighbourhood for a Cu\(^{2+}\) substituent (see Fig. 2) we introduce four basic vectors similarly to conventional ferro- and antiferromagnetic vectors as follows:

\[
F(y) = [S_1 + S_2 + S_3 + S_4]; \quad G(y) = [S_1 - S_2 - S_3 - S_4];
\]

\[
A(y) = [S_1 + S_2 - S_3 - S_4]; \quad C(y) = [S_1 - S_2 - S_3 + S_4]
\]

with a kinematic constraint: \((F \cdot A) = (C \cdot G) = 0\) valid for two identical spirals irrespective of their phase shift. Then the electric polarization induced by the parity-breaking exchange coupling of Cu\(^{2+}\) substituent with a complete set of four neighboring in-chain Cu\(^{2+}\) ions 1-4 (see Fig. 1) can be written as follows:

\[
P_{x,y} = d_{x,y}(s \cdot A); \quad P_{z} = d_{z}(s \cdot C).
\]

Spin polarization of Cu\(^{2+}\) substituent spin can be easily found within the framework of a weak coupling approximation, if one take the most general form of the impurity-spiral ground state \((yy)\) exchange interaction

\[
V_{S} = \sum_{i=1-4} \hat{s}_{i}^{+} (i) \hat{s}_{i} = (s \cdot \hat{H}_{0}), \quad (4)
\]

where \(\hat{H}_{0}\) is an effective magnetic field, acting on the Cu\(^{2+}\) substituent, \(I_{ao}(i) = I_{a}; I_{x} (i) = I_{x}; I_{y} (i) = -I_{xy}(2) = I_{xy}(3) = -I_{xy}(4) = I_{xy}; I_{y} (1) = -I_{y}(2) = I_{y}(3) = -I_{y}(4) = I_{y}\), are a symmetric matrix of the exchange integrals. Thus for the effective field we obtain

\[
\hat{H}_{0}(y) = \hat{I}_{F}F + \hat{I}_{G}G \quad (5)
\]

where

\[
\hat{I}_{F} = \begin{pmatrix} I_{xx} & 0 & I_{xz} \\ 0 & I_{yy} & 0 \\ I_{xz} & 0 & I_{zz} \end{pmatrix}; \quad \hat{I}_{G} = \begin{pmatrix} 0 & I_{xy} & 0 \\ I_{xy} & 0 & I_{yz} \\ 0 & I_{yz} & 0 \end{pmatrix}.
\]

We start with the ab-plane spiral ordering of Cu\(^{2+}\) spins in the CuO\(_2\) chains of LiCuO\(_2\), which deduced from neutron diffraction data in zero external field\(^\text{12}\) and assume \(T = 0\). For zero external magnetic field or for a field directed along the c axis and for \(\alpha = \pm \pi/2\) the electric polarization of the \(y\)-th Cu\(^{2+}\) substituent center oscillates as follows

\[
P_{c}(y) = \frac{8d_{c}uS^{2}}{H(y)}[(I_{xx} - I_{yy})u \cos(2qy) \pm 2I_{xy}v \sin(2qy)], \quad (6)
\]

where \(u = \cos(\frac{q}{2}h), v = \sin(\frac{q}{2}h)\), and for \(h = 0\)

\[
H(y) = 2\sqrt{2S}[I_{xx}^{2} + I_{yy}^{2} + I_{zz}^{2}]u^{2} + (2I_{xy}^{2} + I_{yz}^{2})v^{2}) + 2(I_{xx} + I_{yy}I_{xy} + I_{xx}I_{yz})uv \cos(2qy)
\]

First, it should be noted that the both "left" A-type \((\alpha = \pi/2)\) and "right" B-type \((\alpha = -\pi/2)\) substituent contributions sum to one macroscopic polarization \(P_{c}\). On the other hand, it means that \(P_{a}\) vanishes due to an exact compensation of A-type and B-type contributions since \(d_{e}(A) = -d_{e}(B)\). For \(P_{z}\) we arrive at a strict cancellation of the net electric polarization given \(\alpha = \pm \pi/2\) due to opposite signs of the antisymmetric part of the effective field. Moreover, this cancellation hold itself also under an external magnetic field irrespective of its direction. Second, we note that a nonzero electric polarization for the substituent center 12-Cu\(^{2+}\)-34 can be related only with the anisotropic substituent-spiral exchange coupling. The net polarization \(\langle P_{c}(y)\rangle\) seems to be rather weak because of several reduction effects: i) the existence of non-compensated non-oscillatory contribution of isotropic exchange to the effective magnetic field \((\text{7})\); ii) a quadratic or cubic dependence of \(\langle P_{c}(y)\rangle\) on the exchange anisotropy parameters. In order to demonstrate the role of the anisotropic exchange we adopt a relation between the anisotropy parameters predicted by a simple nearest-neighbor magneto-dipole model:

\[
(I_{xx} - I_{yy}) = 0, (I_{xx} = I_{yy}) = \sqrt{2I_{xy}}. \quad \text{The dependence of} \quad \langle P_{c}(y)\rangle \quad \text{on the ratio} \quad \delta = I_{xy}/I_{xx} \quad \text{appears to be strongly nonlinear, being approximately} \quad \propto \delta^{2}, \quad \text{for a small anisotropy. Only a strong anisotropy} \quad \delta \sim 1 \quad \text{provides the} \quad \text{magnitudes of} \quad \langle P_{c}(y)\rangle \quad \text{comparable with that of} \quad \langle P_{a}(y)\rangle \quad \text{in LiCuVO}_{4}. \quad \text{Typical field dependence of} \quad \langle P_{c}(y)\rangle \quad \text{is shown in Fig. 3} \quad \text{given} \quad QB/2 = 0.172\pi \quad \text{which corresponds to a pitch angle} \quad \approx 62^\circ. \quad \text{12,14}\]

A magnetic field \(h \parallel a\) induces in LiCuO\(_2\) a ab-bc spin-flop transition to the phase with a bc-plane spiral ordering. Interestingly, that irrespective of the field direction a bc-plane spin axial ordering, similarly to that of ab-plane one, supports only a c-axis orientation of both local and net electric polarizations, which expressions can be easily obtained from their ab-axis counterparts,
if one makes the interchange: \( h_x \rightarrow h_z \), \( I_{xy} \leftrightarrow I_{zy} \). It is worth noting that at variance with the \( ab \)-plane spin spiral ordering the \( c \)-axis orientation of net electric polarization for \( bc \)-plane spin arrangement agrees with the predictions of the spin current scenario. Thus both the local \( \mathbf{P}(y) \) and the averaged electric polarizations \( \langle \mathbf{P}(y) \rangle \) for \( ab \) and \( bc \) plane spin spirals lie along the \( c \)-axis even in zero magnetic field. It’s quite another matter for the \( ac \)-plane spin spiral arrangement which can be a result of a spin-flop transition in an external magnetic field directed along \( b \)-axis. Contributions of the \( A \)- and \( B \)-type centers to \( P_a \) and \( P_c \) are strictly opposite in sign, that means their cancellation for \( P_c \) and doubling for \( P_a \). From the other hand, for the first time, the \( P_b \) component of electric polarization appears to be nonzero. Thus, in contrast with two preceding instances both the local \( \mathbf{P}(y) \) and the averaged electric polarizations \( \langle \mathbf{P}(y) \rangle \) for \( ac \)-plane spin spirals lie in \( ab \) plane even in zero magnetic field. Moreover, we arrive at a simple relation between the \( a \)- and the \( b \)-components of the electric polarization: 

\[
P_b/P_a = -v/u = -\tan(qb/2),
\]

that corresponds to \( P_b/P_a \approx -0.6 \) given the pitch angle \( qb \approx 62^\circ \). Fig. 4 shows the field dependence of \( \langle P_{a,b}(y) \rangle \) for \( h \parallel b \) \( (I_{xy}/I_{xz} = 0.4) \) for the \( ac \)-plane spiral.

The mechanism of impure ferroelectricity we discuss does consistently explain all the puzzles of the magnetoelectric effect observed in LiCu$_2$O$_2$ by Park et al. (see Fig. 1). First of all the model explains the \( c \)-axis direction of the spontaneous electric polarization emerging below the spiral-magnetic ordering temperature within the framework of a dominant \( ab \) plane Cu$^{2+}$ spin arrangement, proposed earlier from neutron diffraction data. We argue that an external field \( h \parallel b \) induces spin-flop transition with the Cu$^{2+}$ spin spiral plane flipping from the \( ab \) to the \( ac \) plane accompanied by the flipping of net electric polarization \( \mathbf{P} \) from the \( c \)-axis to the \( ab \)-plane where the relation imbetween \( b \)- and \( a \)-components is determined by the actual pitch angle. The twin structure observed in \( ab \) plane of the LiCu$_2$O$_2$ crystal and ferroelectric domain effect make the field dependence of electric polarization quite complex. Indeed, an external field \( h \parallel b \) induces different spin-flop transitions in different twins: \( ab \rightarrow ac \) and \( ab \rightarrow bc \), respectively. Only in the former twins we deal with \( P_c \rightarrow P_{ab} \) flipping of ferroelectric moment, while in the latter twins the polarization remains oriented along the \( c \)-axis, though having a varied magnitude as compared with the \( ab \) plane spin spiral. Such a behavior is observed in experiments by Park et al. with a relation between the in-plane components of polarization which is close to a theoretically predicted value 0.6. At variance with LiCuVO$_4$ the spontaneous \( (h = 0) \) electric polarization in the low-temperature spiral phase of LiCu$_2$O$_2$ does depend not only on the pitch angle \( qb \) and the relation imbetween the values of exchange anisotropy parameters, but also on the relative magnitude of exchange anisotropy as compared with isotropic exchange. Namely this feature is believed to determine the relatively small magnitude of the multiferroic effect in LiCu$_2$O$_2$ as compared with LiCuVO$_4$.

Thus we conclude that at variance with the relativistic spin current model the nonrelativistic parity breaking exchange induced polarization for the centers formed by Cu$^{2+}$ substituted for Cu$^{1+}$ in nonstoichiometric LiCu$_2$O$_2$ with a simple zero-field \( ab \)-plane spiral ordering can be a natural electronic source of multiferroicity found by Park et al. in this cuprate.

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