Nonrelativistic multiferrocity in the nonstoichiometric spin-$\frac{1}{2}$ spiral-chain cuprate $LiCu_2O_2$

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Puzzling multiferroic behavior observed recently in spin-1/2 one-dimensional chain cuprate $LiCu_2O_2$ with edge-shared arrangement of CuO_4 plaquettes and incommensurate spiral spin ordering is consistently explained to be a result of the nonrelativistic exchange-induced electric polarization on the Cu^{2+} centers substituting for the positions native for the Cu^{1+} ions. These substituent centers are proven to be an effective probe of the spin incommensurability and magnetic field effects.

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Intensive study of magnetoelectric and multiferroic materials is stimulated both by their potential application in novel technological devices and growing interest to fundamental problems of magnetoelectric coupling which proved to be a very sensitive tool to uncover subtle details of interrelation between charge, orbital, and spin ordering. However, due to its complexity, theoretical understanding of the mechanism(s) of strong magnetoelectric coupling is far from being satisfactory. Remarkable demonstration of the present day situation is provided by a hot discussion around recent observations of multiferroic behavior concomitant the incommensurate spin spiral ordering in chain cuprates $LiCuVO_4$ (Refs. 1–3) and $LiCu_2O_2$ (Ref. 4) challenging the multiferroic community. At first sight, these cuprates seem to be prototypical examples of 1D spiral-magnetic ferroelectrics revealing the *relativistic* mechanism of "ferroelectricity caused by spin-currents[5]" 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[6] 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.[5] However, both systems reveal a mysterious behavior with conflicting results obtained by different groups. Indeed, Yasui *et al.*[2] claim the $LiCuVO_4$ reveals clear deviations from the predictions of spin-current models[5,6] while Schrettle *et al.*[3] assure its applicability. In contrast to $LiCuVO_4$, the $LiCu_2O_2$ shows up a behavior which is obviously counterintuitive within the framework of spiral-magnetic ferroelectricity.[4] It is worth noting that at variance with Park *et al.*,[4] Naito *et al.*[1] have not found any evidence for ferroelectric anomalies in $LiCu_2O_2$. Such a discrepancy one observes in microscopic model approaches as well. The relativistic LSDA calculations[7] seemingly explain the $LiCuVO_4$ data[3] but fail in case of $LiCu_2O_2$. 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 $LiCu_2O_2$ shows that the in-chain spin current does not produce an electric polarization because of an exact cancellation of two Cu-O-Cu paths.[8] Moreover, recently we have shown[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 $LiCu_2O_2$.

$LiCu_2O_2$ is orthorhombic mixed-valent compound with copper ions in the Cu^{2+} and Cu^{1+} valence states.[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 $LiCu_2O_2$ was obtained independently by Gippius *et al.*[11] and Masuda *et al.*[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[12] thus forming ab-plane spin spirals running along **b** axis:$\mathbf{S}(y)=S(\cos\theta,\sin\theta,0)$, where $\theta=qy+\alpha$, α is a phase shift.

Park *et al.*[4] have found that the incommensurate spin ordering in $LiCu_2O_2$ 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.[12] When a magnetic field applied along the **b** axis (see Ref. 4 for the making use of a,b notations in ab-twinned crystal), P_c decreases and P_a increases, implying

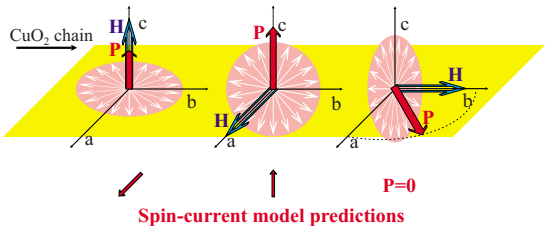

FIG. 1. (Color online) Direction of ferroelectric polarization in $LiCu_2O_2$ for different spin spiral plane orientation.

that the Cu^{2+} spin spiral plane flips from the *bc* to *ab* plane, resulting in a flip of the polarization from the *c* to *a* axis. It is expected that $\mathbf{h}\|\mathbf{c}$ may flip the spiral plane from the *bc* to *ab* plane, so that **P** may flip from the **c** to **a** axis with h_c. However, this is completely in contrast with the observations[4] that h_c enhances P_c and h_b is the one inducing the **P** flip from the **c** to **a** axis. The appearance of P_a with h_a is also counterintuitive within the framework of the relativistic spiral-magnetic ferroelectricity.[5,6] These unexpected magnetic field effects raise doubts about the validity of the scenario of relativistic spin current spiral-magnetic ferroelectricity and point to another, probably the out-of-spin-chain origin of the magnetoelectric coupling.

In this connection it is worth noting that the thermogravimetric analysis revealed that the $LiCu_2O_2$ samples had a lower content of Cu ions than follows from the stoichiometric formula.[12] Chemical disorder and a Cu deficiency by as much as $x=16\%$ are inherently present. The "surplus" Li^+ ions in $LiCu_2O_2$ occupy Cu^{2+} sites, due to a good match of ionic radii (0.68 and 0.69 Å, respectively). The charge compensation requires that the introduction of nonmagnetic Li^+ ions into the double chains is accompanied by a transfer of the spin-1/2 carrying Cu^{2+} ions onto the Cu^+ interchain sites.[12] At first sight it seems improbable because of different coordination preferences. However, the actual coordination of the native Cu^+ interchain site approaches most likely an axially distorted square, or rhombic coordination due to an extremely small interdumbbell separation ($d\approx 2.86$ Å) as compared with other O-Cu^+-O dumbbell bearing compounds (e.g., YBa_2CuO_6, $d\approx 3.8$ Å).[13] In other words, the Zhang-Rice singlet within the CuO_2 chains becomes unstable with respect to a hole transfer to one of the neighboring Cu^+ sites. Details of this instability will be discussed elsewhere. If the doped hole would be remain 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^+ interchain sites? Purely electrostatic arguments made within the framework of the point-charge model, supported by account for Cu 3*d*-O 2*p* covalency, point to a competition of d_{z^2} and d_{yz} orbitals while strong intra-atomic s-d_{z^2} 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[14] with Cu^{2+} spin spirals explains all the puzzles observed by Park *et al.*[4] 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 3*d* centers we will 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:

$$\hat{V}_{\rm ex} = \sum_n \hat{I}(\mathbf{R}_n)(\mathbf{s}\cdot\mathbf{S}_n), \tag{1}$$

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

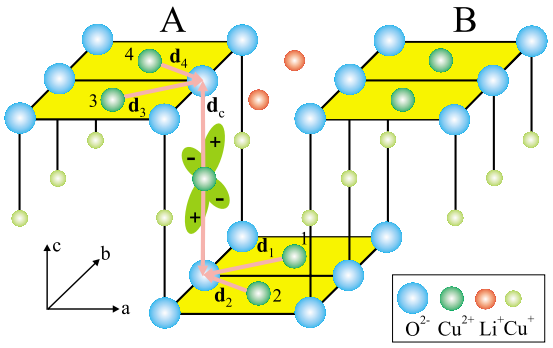

FIG. 2. (Color online) An idealized view of crystal structure of $LiCu_2O_2$ (upper bilayer). A "left" site impurity center with Cu^{2+} ion substituted for Cu^{1+} ion is in between upper and lower CuO_2 chains from the same unit cell. Shown is the hole density distribution in d_{yz} orbital. The exchange-induced dipole moments are shown by arrows.

$$\hat{I}(\mathbf{R}_n) = \begin{pmatrix} I_{gg}(\mathbf{R}_n) & I_{gu}(\mathbf{R}_n) \\ I_{ug}(\mathbf{R}_n) & I_{uu}(\mathbf{R}_n) \end{pmatrix}. \tag{2}$$

The conventional diagonal *gg* part of the exchange coupling does spin-polarize the ground state, while the parity-breaking off-diagonal *gu* part does 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,

$$\mathbf{P} = 2c_{gu}\langle g|e\mathbf{r}|u\rangle = \sum_n \mathbf{\Pi}_n(\mathbf{s}\cdot\mathbf{S}_n), \tag{3}$$

with $\mathbf{\Pi}_n = 2I_{gu}(\mathbf{R}_n)\langle g|e\mathbf{r}|u\rangle/\Delta_{ug}$ ($\Delta_{ug}=\epsilon_u-\epsilon_g$). Thus, the spin-dependent electric polarization emerges as a combined effect of the two, *gg* and *gu* exchange couplings. 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 neighboring Cu^{2+} substituent (hole ground state $|g\rangle \propto d_{yz}$) will result in the *ab*-plane electric polarization of CuO_4 chain plaquettes and the *c*-axis polarization of the Cu^{2+} substituent.

Unit cell of $LiCu_2O_2$ contains two types (left and right) of native Cu^{1+} positions (see Fig. 1) with four neighboring 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 CuO_2 chain belonging to the adjacent bilayer. According to local-density approximation (LDA) calculation there is practically no hybridization with that chain.[11]

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

$$\mathbf{F}(y) = [\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4]; \quad \mathbf{G}(y) = [\mathbf{S}_1 - \mathbf{S}_2 + \mathbf{S}_3 - \mathbf{S}_4];$$

$$\mathbf{A}(y) = [\mathbf{S}_1 + \mathbf{S}_2 - \mathbf{S}_3 - \mathbf{S}_4]; \quad \mathbf{C}(y) = [\mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3 + \mathbf{S}_4]$$

with a kinematic constraint: $(\mathbf{F}\cdot\mathbf{A})=(\mathbf{C}\cdot\mathbf{G})=0$ 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:

$$P_{a,c} = d_{a,c}(\mathbf{s}\cdot\mathbf{A}); \quad P_b = d_b(\mathbf{s}\cdot\mathbf{C}). \tag{4}$$

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 ($I_{gg}=I$) exchange interaction,

$$V_{sS} = \sum_{i=1-4} \hat{\mathbf{s}}\overleftrightarrow{\mathbf{I}}(i)\hat{\mathbf{S}}_i = (\hat{\mathbf{s}}\cdot\hat{\mathbf{H}}_0), \tag{5}$$

where $\hat{\mathbf{H}}_0$ is an effective magnetic field, acting on the Cu^{2+} substituent, $I_{\alpha\alpha}(i)=I_{\alpha\alpha}$, $I_{xz}(i)=I_{xz}$; $I_{xy}(1)=-I_{xy}(2)=I_{xy}(3)=-I_{xy}(4)=I_{xy}$; $I_{zy}(1)=-I_{zy}(2)=I_{zy}(3)=-I_{zy}(4)=I_{zy}$ form a symmetric matrix of the exchange integrals. Thus, for the effective field we obtain

$$\mathbf{H}_0(y) = \overleftrightarrow{\mathbf{I}}_\mathbf{F}\mathbf{F} + \overleftrightarrow{\mathbf{I}}_\mathbf{G}\mathbf{G}, \tag{6}$$

with

$$\overleftrightarrow{\mathbf{I}}_\mathbf{F} = \begin{pmatrix} I_{xx} & 0 & I_{xz} \\ 0 & I_{yy} & 0 \\ I_{xz} & 0 & I_{zz} \end{pmatrix}; \quad \overleftrightarrow{\mathbf{I}}_\mathbf{G} = \begin{pmatrix} 0 & I_{xy} & 0 \\ I_{xy} & 0 & I_{zy} \\ 0 & I_{zy} & 0 \end{pmatrix}.$$

Upon comparing Eqs. (4) and (5), we see that the electrical polarization on the Cu^{2+} substituent center emerges only for a very specific spin surroundings. Interestingly, regular CuO_2 chains spin polarized in *ab* plane induce on these Cu^{2+} centers a spin polarization along all the *a*, *b*, and *c* axes, that can explain some seemingly inconsistencies found recently in neutron-diffraction and x-ray scattering data[15,16] but without all-out negation of *ab*-planar CuO_2 spiral. We start with a zero external field *ab*-plane spiral ordering of Cu^{2+} spins in the CuO_2 chains of $LiCu_2O_2$, as deduced from first neutron-diffraction data[12] supported by later electron-spin resonance (ESR) data,[17] 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:

$$P_c(y) = \frac{8d_c u S^2}{H(y)}[(I_{xx}-I_{yy})u\cos(2qy) \pm 2I_{xy}v\sin(2qy)], \tag{7}$$

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

$$H(y) = 2\sqrt{2}S[(I_{xx}^2+I_{yy}^2+I_{zx}^2)u^2 + (2I_{xy}^2+I_{zy}^2)v^2] + 2[(I_{xx}+I_{yy})I_{xy}+I_{zx}I_{zy}]uv\cos(2qy) \mp \{[(I_{xx}+I_{yy})(I_{xx}-I_{yy})+I_{zx}^2]u^2 - I_{zy}^2v^2\}\sin(2qy)]^{1/2}. \tag{8}$$

First, it should be noted that the both "left" A-type ($\alpha=\pi/2$) and "right" B-type ($\alpha=-\pi/2$) substituent positions contribute equally to a 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 $d_a(A)=-d_a(B)$. For P_b 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_A^{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 noncompensated nonoscillatory contribution of isotropic exchange to the effective magnetic field [Eq. (8)]; (ii) a quadratic or cubic dependence of $\langle P_c(y)\rangle$ on the exchange anisotropy parameters.

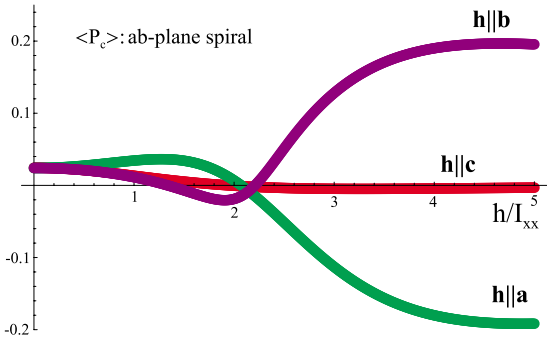

FIG. 3. (Color online) The field dependence of $\langle P_c(y)\rangle$ (in units of d_c) for *ab*-plane spiral: $I_{xy}/I_{xx}=0.4$.

In order to demonstrate the role of the anisotropic exchange we adopt a relation between the anisotropy parameters predicted by a simple nearest-neighbor magnetodipole model: $(I_{xx}-I_{yy})=0$, $(I_{zx}=I_{zy})=\sqrt{2}I_{xy}$. The dependence of $\langle P_c(y)\rangle$ on the ratio $\delta=I_{xy}/I_{xx}$ appears to be strongly nonlinear, being approximately $\propto\delta^3$ for a small anisotropy. Only a strong anisotropy $\delta\sim 1$ provides the magnitudes of $\langle P_c(y)\rangle$ comparable with that of $\langle P_a(y)\rangle$ in $LiCuVO_4$. The typical field dependence of $\langle P_c(y)\rangle$ is shown in Fig. 3 given $qb/2=0.172\pi$ which corresponds to a pitch angle $\approx 62°$.[12,18]

A magnetic field $\mathbf{h}\|\mathbf{a}$ induces in $LiCu_2O_2$ 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 spiral 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: $h_x \to h_z$, $I_{xy} \leftrightarrow I_{zy}$. 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 is 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, which

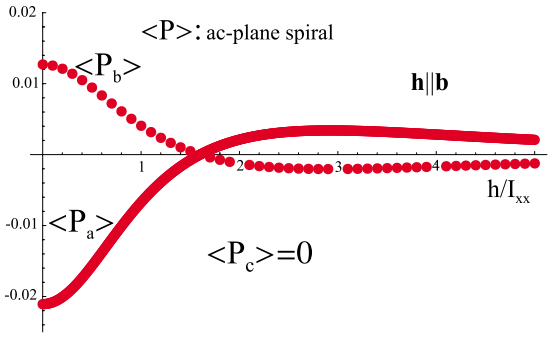

FIG. 4. (Color online) The field dependence of $\langle P_{a,b}(y)\rangle$ (in units of d) for $\mathbf{h}\|\mathbf{b}(I_{xy}/I_{xx}=0.4)$ for the ac-plane spiral.

means their cancellation for P_c and doubling for P_a. On 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: $P_b/P_a=-v/u=-\tan(qb/2)$, which corresponds to $P_b/P_a\approx-0.6$ given the pitch angle $qb\approx62°$. Figure 4 shows the field dependence of $\langle P_{a,b}(y)\rangle$ for $\mathbf{h}\|\mathbf{b}$ $(I_{xy}/I_{xx}=0.4)$ for the ac-plane spiral.

The mechanism of impure ferroelectricity we discuss does consistently explain all the puzzles of the magnetoelectric effect observed in $LiCu_2O_2$ by Park *et al.*[4] (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.[12] We argue that an external field $\mathbf{h}\|\mathbf{b}$ 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 in between b and a components is determined by the actual pitch angle. The twin structure observed in ab plane of the $LiCu_2O_2$ crystal and the ferroelectric domain effects[4] make the field dependence of electric polarization quite complex. Indeed, an external field $\mathbf{h}\|\mathbf{b}$ 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.*[4] 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 $LiCu_2O_2$ does depend not only on the pitch angle (qb) and the relation in between 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 $LiCu_2O_2$ as compared with $LiCuVO_4$.[1] All these results agree completely with experimental findings by Park *et al.*[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 $LiCu_2O_2$ with a simple zero-field ab-plane spiral ordering can be a natural electronic source of multiferroicity found by Park *et al.*[4] in this cuprate.

Our results raise a number of questions of great importance for physics of magnetism and multiferroicity in the spin-1/2 quantum matter of $LiCu_2O_2$. Should a multiferroic behavior be observed in a stoichiometric $LiCu_2O_2$ with a regular arrangement of Cu^{2+} and Cu^{1+} ions? What role do the centers formed by Cu^{2+} substituted for Cu^{1+} in magnetism of $LiCu_2O_2$ play, in particular, in magnetic anisotropy? In this connection it is worth noting an isostructural stoichiometric cuprate $NaCu_2O_2$ where the ^{23}Na NMR line-shape analysis[19] points to an incommensurate spin structure consistent with a spiral modulation of the Cu magnetic moments polarized in the bc plane in contrast with the ab-plane polarization reported for nonstoichiometric $LiCu_2O_2$. It is the first experimental indication for a polarization in an edge-shared cuprate with spins lying in a plane perpendicular to the plane of the basic CuO_4 plaquette.

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