Microscopic mechanisms of spin-dependent electric polarization in 3d oxides

A.S. Moskvin\textsuperscript{1} and S.-L. Drechsler\textsuperscript{2}

\textsuperscript{1} Ural State University, 620083 Ekaterinburg, Russia
\textsuperscript{2} Leibniz Institut f"ur Festk"orper- und Werkstoffforschung Dresden, D-01171, Dresden, Germany

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Abstract. We present a short critical overview of different microscopic models for nonrelativistic and relativistic magnetoelectric coupling including the so-called "spin current scenario", \textit{ab-initio} calculations, and several recent microscopic approaches to a spin-dependent electric polarization in 3d oxides.

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1 Introduction

Since Astrov’s discovery of the magnetoelectric (ME) effect in Cr$_2$O$_3$,\textsuperscript{11} several microscopic mechanisms of magnetoelectric coupling were proposed,\textsuperscript{2} however, the multiferroicity (see e.g., Refs.\textsuperscript{3} and review articles Refs.\textsuperscript{4}) has generated an impressive revival of the activity in the field. The microscopic origin of the magnetically driven electric polarization is the topic of an intense and controversial debate. Currently two essentially different spin structures of net electric polarization in crystals are considered: a bilinear \textit{nonrelativistic symmetric} spin coupling

\[ P_s = \sum_{mn} \Pi_{mn} \left( S_m \cdot S_n \right) \]  \hspace{1cm} (1)

and a bilinear \textit{relativistic antisymmetric} spin coupling

\[ P_a = \sum_{mn} \Pi_{mn} \left( S_m \times S_n \right) \]  \hspace{1cm} (2)

respectively. If the first term stems somehow or other from a spin isotropic Heisenberg exchange interaction, the second term does from antisymmetric Dzyaloshinsky-Moriya (DM) coupling. These effective spin-operator forms do not discriminate the "ionic" and "electronic" contributions to magnetically driven ferroelectricity related with the off-center ionic displacements and the electron density redistribution, respectively. A microscopic quantum theory of the ME effect has not yet been fully developed, although several scenarios for particular materials have been proposed. Many authors consider that the giant multiferroicity requires the existence of sizeable atomic displacements and structural distortions driven by isotropic symmetric exchange coupling\textsuperscript{5,9,7} or antisymmetric DM coupling\textsuperscript{8} ignoring, however, the fact that the effects of nuclear displacements and electron polarization should be described on equal footing, e.g., in frames of the well-known shell model of Dick and Overhauser\textsuperscript{9} widely used in lattice dynamics. Shell and core displacements may be of a comparable magnitude. The conventional shell model does not take into account the spin and orbital degrees of freedom, hence it cannot describe the multiferroic effects. In fact, the displacements of both the atomic core and electron shell would depend on the spin surroundings producing an synergetic effect of spin-dependent electric polarization. Obviously, this effect manifest itself differently in neutron and x-ray diffraction experiments. Sorting out two contributions is a key issue in the field.

The second harmonic generation (SHG) spectroscopy reveals a giant effect in compounds with magnetically driven ferroelectricity (ThMn$_2$O$_5$, MnWO$_4$) thus pointing to an electronic rather than ionic origin of the spontaneous polarization\textsuperscript{10}. Interestingly, the exchange-induced electric dipole moment \textsuperscript{1}, derived many years ago \textsuperscript{11} (see, also Ref.\textsuperscript{12}), seems to be a natural electronic mechanism for giant multiferroicity. However, the second, or exchange-relativistic electric dipole moment \textsuperscript{2}, despite its visible weakness, is at present frequently addressed to be the leading contributor to electronic multiferroicity, mainly due to the so-called "spin-current" mechanism\textsuperscript{13,14}. To a large extent it is explained by two reasons. First, in a most part of multiferroics the electric polarization is observed when the magnetic ordering is of a type that breaks chiral symmetry, e.g., spiral or helical order with a nonzero "spin-current" \[ a \propto [S_m \times S_n] \times [S_m \times S_n] \]. Second, such a mechanism allows us to easily predict the direction of the ferroelectric polarization for certain helical spin structures: \[ a \propto \sum_{mn} [R_{mn} \times [S_m \times S_n]] \] \[ \langle (I_{mn})_{ij} \propto \epsilon_{ijk} [R_{mn} \times [S_m \times S_n]] \rangle \] or \[ a \propto e \times Q \] (\( e \) is the helix spin rotation axis, \( Q \) is the helix wave vector)\textsuperscript{14}. It is worth noting that phenomenological theory by Mostovoy\textsuperscript{13} implies a coexistence of two independent order parameters.
The ME coupling parameter $\Phi_{\text{ME}}(P(r), M(r)) = \gamma P \cdot (\nabla \cdot M) - (M \cdot \nabla)M$, while for the multiferroics under consideration we deal with $M(r)$ to be a leading, or first order parameter, and $P(r)$ as a second order parameter which is expressed in terms of the former one. Furthermore, his phenomenological theory does not explain neither the origin nor the magnitude of the ME coupling parameter $\gamma$.

"Ferroelectricity caused by spin-currents" has established itself as one of the leading paradigms for both theoretical and experimental investigations in the field of strong multiferroic coupling. However, a "rule" that chiral symmetry needs to be broken in order to induce a ferroelectric moment at a magnetic phase transition is questionable [15]. There are notable exceptions, in particular, a magnetic chiral symmetry breaking [16,17], and delafossite CuFe$_1$-$\delta$Al$_2$O$_2$, where the helimagnetic ordering generates a spontaneous electric polarization parallel to the helical axis [17], in sharp contrast with the prediction of the spin current model. Moreover, there are increasing doubts whether weak exchange-relativistic coupling can generate the giant electric polarization observed in some multiferroics.

Another point of hot debates around the microscopic origin of ME coupling is related with recent observations of a multiferroic behaviour concomitant the incommensurate spin spiral ordering in chain cuprates LiVCuO$_4$ [18,19] and LiCu$_2$O$_2$ [21,22,29]. 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" [13]. However, these, in particular, LiCu$_2$O$_2$ show up a behavior which is obviously counterintuitive within the framework of spiral-magnetic ferroelectricity [21]. Furthermore, quantum helimagnets NaCu$_2$O$_2$ and Li$_2$ZrCuO$_4$ with a very similar CuO$_2$ spin chain arrangement do not reveal signatures of a multiferroic behavior. Thus, there is no clear understanding standing all these striking properties.

Despite its popularity, the original "spin-current" model and its later versions [21,22,29] (see also Ref. [26]) seem to be questionable as the authors proceed with an unrealistic scenario. Indeed, when addressing a generic centrosymmetric $M_1$-$O$-$M_2$ system they groundlessly assume an effective spin polarization Zeeman field $\mu m$ (m, is a local magnetic moment) to align noncollinearly the spins of 3d electrons and to provide a nonzero value of the two-site spin current $[S_1 \times S_2]$. The energy separation $U$ originates from the local Coulomb repulsion and the Hund coupling in the magnetically ordered phase [13,21,22,26]. Such an assumption goes beyond all the thinkable perturbation schemes and leads to an unphysically large effect of breaking of a spatial symmetry induced by a spin configuration that manifests itself in an emergence of a nonzero electric dipole moment for an isolated centrosymmetric $M_1$-$O$-$M_2$ system [13].

Size of the macroscopic polarization $P$ in nonmagnetic ferroelectrics computed by modern ab-initio band structure methods agrees exceptionally well with the ones observed experimentally. However, the state of the art ab-initio computations for different multiferroics: manganites HoMnO$_3$ [27], TbMn$_2$O$_5$ [28], HoMn$_2$O$_5$ [29], spin spiral chain cuprates LiVCuO$_4$ and LiCu$_2$O$_2$ [30] yield data spread within one-two orders of magnitude with ambiguous and unreasonable values of polarization depending on whether these make use of theoretical or experimental structural data or different values of the correlation parameters. The basic starting points of the current versions of such spin-polarized approaches as the LSDA seem to exclude any possibility to obtain a reliable quantitative estimation of the spin-dependent electric polarization in multiferroics [31]. We should emphasize two weak points of so-called first-principle calculations which appear as usual to be well forgotten in the literature. First, these approaches imply the spin configuration induces immediately the appropriate breaking of spatial symmetry that makes the symmetry-breaking effect of a spin configuration to be unphysically large. It is worth noting that the spin-current scenario [13] starts with the same LSDA-like assumption of unphysically large symmetry-breaking spin-magnetic field. Conventional schemes imply just the opposite, however, a physically more reasonable picture when the charge and orbital anisotropies induce a spin anisotropy. Second, the first-principle calculations neglect quantum fluctuations, that restricts drastically their applicability to a correct description of the ME coupling derived from the high-order perturbation effects.

Below we present a short overview of different microscopic approaches to spin-dependent electric polarization. In Sec.II we address a systematic standard microscopic theory which implies the derivation of effective spin operators for nonrelativistic and relativistic contributions to electric polarization of the generic three-site two-hole cluster such as Cu$1$-$O$-$Cu$2. In Sec.III we address an alternative approach based on the parity breaking exchange coupling and the exchange-induced electric polarization effects. Sec.IV is focused on the microscopic origin of the multiferroic behaviour observed in the edge-shared CuO$_2$ chain compounds LiVCuO$_4$ and LiCu$_2$O$_2$. In Sec.V we draw attention to anomalous magnetoelectric properties of the electron-hole dimers to be precursors of the disproportionated phase which droplets can survive even in nominally pure undoped manganites.

### 2 Spin-dependent electric polarization in a three-site $M_1$-$O$-$M_2$ cluster

Generic three-site $M_1$-$O$-$M_2$ cluster forms a basic element of the crystalline and electron structure of 3d oxides. A realistic perturbation scheme needed to describe properly the active M 3d and O 2p electron states implies strong intra-atomic correlations, the comparable effect of crystal field, the quenching of orbital moments by a low-symmetry crystal field, account for the dp-transfer up to the fourth order effects, and a rather small spin-orbital coupling. To this end we make use of a technique suggested in refs. [32,33].
2.1 Three-site two-hole M$_1$-O-M$_2$ cluster

For illustration, below we address a three-site (Cu$_1$-O-Cu$_2$) two-hole system typical for cuprates with a tetragonal Cu 3d on-site symmetry and a Cu 3d$_{z^2-r^2}$ ground states. We start with the construction of the spin-singlet and spin-triplet wave functions for the system taking account of the p-d hopping, on-site hole-hole repulsion, and crystal field effects for excited configurations $\{\eta\}$ (011, 110, 020, 200, 002) with different hole occupation of Cu$_1$, O, and Cu$_2$ sites, respectively. The p-d hopping for Cu-O bond implies a conventional Hamiltonian

$$H_{pd} = \sum_{\alpha \beta} t_{pd\beta} \tilde{p}_\alpha^\dagger \tilde{d}_\beta + h.c.,$$

where $\tilde{p}_\alpha^\dagger$ creates a hole in the $\alpha$ state on the oxygen site, while $\tilde{d}_\beta$ annihilates a hole in the $\beta$ state on the copper site; $t_{pd\beta}$ is a p-d-transfer integral. For basic 101 configurations with two d$_{z^2-r^2}$ holes localized on its parent sites we arrive at a perturbed wave function as follows

$$\psi_{101;SM} = \eta_S \psi_{101;SM} + \sum_{\{\eta\}_1 \neq 101} c_{\eta}(S\Gamma) \psi_{\{\eta\}S\Gamma SM},$$

where the summation runs both on different configurations and different orbital $\Gamma$ states;

$$\eta_S = [1 + \sum_{\{\eta\}} c_{\{\eta\}}(S\Gamma)^2]^{-1/2}$$

is a normalization factor. It is worth noting that the probability amplitudes, or hybridization parameters, $c_{\{\eta\}1}$, $c_{\{\eta\}10}$ $c_{\{\eta\}20}$, $c_{\{\eta\}02}$, and $t_{pd\beta}^2$, account for relativistic effects in the three-site cluster one should incorporate the spin-orbital coupling $V_{so} = \sum_n \xi_n(l_1 \cdot s_1)$ both for 3d- and 2p-holes with a single particle constant $\xi_n > 0$ for electrons and $\xi_n < 0$ for holes.

In terms of the hole spins the conventional bilinear spin Hamiltonian for the Cu$_1$-O-Cu$_2$ system reads as follows:

$$H_s(12) = J \hat{s_1} \cdot \hat{s_2} + D \cdot (\hat{s_1} \times \hat{s_2}) + \hat{s_1} \hat{s_2} \cdot \hat{K},$$

where $J \propto t_{pd}^4$ is an exchange integral, $D \propto t_{pd}^4 \xi_n$ is a Dzyaloshinsky vector, $\hat{K} \propto t_{pd}^4 \xi_n^2$ is a symmetric second-rank tensor of the anisotropy constants [32,33].

2.2 Nonrelativistic mechanism of spin-dependent electric polarization: local and nonlocal terms

Projecting the electric dipole moment $\mathbf{P} = |e|(\mathbf{r}_1 + \mathbf{r}_2)$ on the spin singlet or triplet ground state of the two-hole system we arrive at an effective electric polarization of the three-center system $\langle \mathbf{P}_{S}\rangle = \psi_{101;SM} \mathbf{P} \psi_{101;SM}$ to consist of local and nonlocal terms, which accomodate the diagonal and off-diagonal on the ionic configurations matrix elements, respectively [31]. The local contribution describes the redistribution of the local on-site charge density and can be written as follows:

$$\langle \mathbf{P}_{S}\rangle_{local} = |e| \eta_S \left[ |\mathbf{R}_1 + \mathbf{R}_2 + (\mathbf{R}_1 + \mathbf{R}_O) \sum_{\Gamma} c_{110}(S\Gamma)|^2 + |\mathbf{R}_O + \mathbf{R}_2 \sum_{\Gamma} c_{011}(S\Gamma)|^2 + 2 |\mathbf{R}_O \sum_{\Gamma} c_{020}(S\Gamma)|^2 + 2 |\mathbf{R}_2 \sum_{\Gamma} c_{200}(S\Gamma)|^2 \right] \mathbf{P}_0,$$

where $\mathbf{P}_0 = |e|(\mathbf{R}_1 + \mathbf{R}_2)$ is a bare purely ionic two-hole dipole moment. Obviously, the net local electric polarization depends only on $\mathbf{R}_1$ vectors (R10, R20, R12). It is worth noting that the net local electric polarization lies in the Cu$_1$-O-Cu$_2$ plane. The nonlocal, or overlap contribution is related with the off-diagonal two-site matrix elements of $\mathbf{P}$ [31].

The effective electric polarization differs for the singlet and triplet pairing due to a respective singlet-triplet difference in the hybridization amplitudes $c_{\{\eta\}S\Gamma}$. Hence may introduce an effective nonrelativistic exchange-dipole spin operator $\hat{P}_s = \Pi(\hat{s}_1 \cdot \hat{s}_2)$ with an exchange-dipole moment

$$\Pi = \langle \mathbf{P}\rangle_t - \langle \mathbf{P}\rangle_s,$$

which can be easily deduced from Exp. [7]. The effective nonrelativistic exchange-dipole moment is determined by competitive local and nonlocal contributions of several configurations [31]. It is worth noting that for the collinear Cu$_1$-O-Cu$_2$ bonding both contributions vanish. As a whole, the exchange-dipole moment vanishes, if the M$_1$-O-M$_2$ cluster has a center of symmetry.

It is worth noting that we addressed only the charge density redistribution effects for Cu 3d and O 2p states and neglected a direct electronic polarization effects for Cu 3d- and O 2p-holes with a single particle constant $\xi_n > 0$ for electrons and $\xi_n < 0$ for holes.

2.3 Relativistic mechanism of the spin-dependent electric polarization

At variance with a scenario by Katsura et al. [13] we have applied a conventional procedure to derive an effective spin operator for a relativistic contribution to the electric dipole moment in the three-site M1-O-M2 system like a technique suggested in references [32,33] to derive expressions for the Cu and O spin-orbital contributions to the DM coupling in cuprates.

The spin-orbital coupling $V_{SO}$ for copper and oxygen ions drives the singlet-triplet mixing which gives rise to a relativistic contribution to electric polarization deduced
from an effective spin operator, or an exchange-relativistic-dipole moment

$$\hat{\mathbf{P}} = \frac{1}{2} \hat{\Pi} \mathbf{T} = \hat{\Pi} \left( \mathbf{s}_1 \times \mathbf{s}_2 \right),$$

(10)

where

$$\Pi_{ij} = -i \langle \Psi_s | \mathbf{P}_i | \Psi_s \rangle = \left( \langle \Phi_s | \mathbf{P}_i | \Phi_s \rangle - \langle \Phi_t | \mathbf{P}_i | \Phi_t \rangle \right) \frac{D_j}{J}$$

(11)

is an exchange-relativistic-dipole tensor ($\Psi_s$ and $\Psi_t$ are spin singlet and spin triplet wave functions [4], respectively). It is easy to see that this quantity has a clear physical meaning to be in fact a dipole matrix element for a singlet-triplet electro-dipole transition in our three-site cluster. Taking into account equation (9), we arrive at a simple form for the exchange-relativistic-dipole moment as follows

$$\hat{\mathbf{P}} = -\frac{1}{J} \hat{\Pi} \left( \mathbf{D} \cdot \left[ \mathbf{s}_1 \times \mathbf{s}_2 \right] \right).$$

(12)

It is worth noting that this vector lies in the Cu$_1$-O-Cu$_2$ plane and its direction, at variance with the spin-current model [13], does not depend on the spin configuration. Furthermore, we see that the both nonrelativistic and relativistic contributions to effective dipole moment in the Cu$_1$-O-Cu$_2$ system have the same direction: $\mathbf{P}_{sa} \propto \hat{\Pi}_s$. In other words, in the both cases the spin-correlation factors, ($\mathbf{s}_1 \times \mathbf{s}_2$) and ($\mathbf{s}_1 \times \mathbf{s}_2$), do modulate a pre-existing dipole moment. The DM type exchange-relativistic-dipole moment [12] is believed to be a dominant relativistic contribution to the electric polarization in a Cu$_1$-O-Cu$_2$ cluster. It is worth noting that the exchange-dipole moment operator $\hat{\mathbf{S}}$ and exchange-relativistic-dipole moment operator [12] are obvious counterparts of the Heisenberg symmetric exchange and DM antisymmetric exchange, respectively. Hence, the Moriya like relation $|\Pi_{ij}| = \frac{\Delta g/g}{|\Pi|}$ seems to be a reasonable estimation for the resultant relativistic contribution to electric polarization in M$_1$-O-M$_2$ clusters. At present, it is a difficult and, probably, hopeless task to propose a more reliable and so physically clear estimate. Taking a typical value of $\Delta g/g \sim 0.1$ we estimate the maximal value of $|\Pi_{ij}|$ as $10^{-3}|e|A(\sim 10^2\mu C/m^2)$ that points to the exchange-relativistic mechanism to be a weak contributor to a giant multiferroicity with ferroelectric polarization of the order of $10^3\mu C/m^2$ as in TbMnO$_3$ [3], though it may be a noticeable contributor in, e.g., Ni$_3$V$_2$O$_8$ [26].

3 Parity breaking exchange coupling and exchange-induced electric polarization

Along with many advantages of the three-site cluster model it has a clear imperfection not uncovering a direct role played by exchange coupling as a driving force to induce a spin-dependent electric polarization. Below we’ll address an alternative approach starting with a spin center such as a MeO$_n$ cluster in 3d oxides exchange-coupled with a magnetic surroundings. Then the magnetoelastic coupling can be related to the spin-dependent electric fields generated by the spin surroundings in a magnetic crystal. In this connection we should point out some properties of exchange interaction that usually are missed in conventional treatment of Heisenberg exchange coupling. Following the paper by Tanabe et al. [11] (see, also Ref. [12]) we do start with a simple introduction to exchange-induced electric polarization effects.

Let address the one-particle (electron/hole) center in a crystallographically centrosymmetric position of a magnetic crystal. Then all the particle states can be of a certain 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 to only one excited odd-parity state $|u\rangle$. The exchange coupling with the surrounding spins can be written as follows:

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

(13)

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

$$\hat{I}(\mathbf{R}_n) = \left( \begin{array}{cc} I_{g\delta}(\mathbf{R}_n) & I_{g\alpha}(\mathbf{R}_n) \\ I_{u\delta}(\mathbf{R}_n) & I_{u\alpha}(\mathbf{R}_n) \end{array} \right).$$

(14)

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

$$\mathbf{P} = \sum_n \Pi_n (\mathbf{s} \cdot \mathbf{S}_n),$$

(15)

where

$$\Pi_n = 2I_{g\delta}(\mathbf{R}_n) \frac{\langle g| \mathbf{e} \mathbf{r} | u \rangle}{\Delta_{ug}}$$

(16)

with $\Delta_{ug} = \epsilon_u - \epsilon_g$. It is easy to see that in frames of a mean-field approximation the nonzero dipole moment shows up only for spin-noncentrosymmetric surroundings, that is if the condition $\langle \mathbf{S}(\mathbf{R}_n) \rangle = \langle \mathbf{S}(-\mathbf{R}_n) \rangle$ is broken. For an isotropic bilinear exchange coupling this implies a spin frustration.

It should be noted that at variance with the spin-current model [13] the direction of the exchange-induced dipole moment for $i, j$ pair does not depend on the direction of spins $\mathbf{S}_i$ and $\mathbf{S}_j$. In other words, the spin-correlation factor $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ modulates a pre-existing dipole moment $\Pi$, which direction and value depend on the Me$_i$-O-Me$_j$ bond geometry and orbitals involved in the exchange coupling.

The magnitude of the off-diagonal exchange integrals can sufficiently exceed that of a conventional diagonal exchange integral. Given reasonable estimations for the off-diagonal exchange integrals $I_{ug} \approx 0.1 \, \text{eV}$, the $u - g$ energy separation $\Delta_{ug} \approx 2 \, \text{eV}$, the dipole matrix element $|\langle g| \mathbf{e} \mathbf{r} | u \rangle| \approx 0.1 \, \text{A}$, spin function $|\langle \mathbf{s}, \mathbf{S}_n \rangle| \approx 1$ we arrive at an estimation of the maximal value of the electric polarization: $P \approx 10^2 \, \mu \text{C/m}^2$. This estimate points to the exchange-induced electric polarization to be potentially the most significant source of magnetoelastic coupling for new giant multiferroics. It is worth noting that the exchange-induced polarization effect we consider
is particularly strong for the 3d clusters such as MeO₃ with an intensive low-lying electro-dipole allowed transition |g⟩ → |u⟩ which initial and final states are coupled due to a strong exchange interaction with a spin surroundings [37]. This simple rule may be practically used to search for new multiferroic materials.

The parity-breaking exchange coupling can produce a strong electric polarization of oxygen ions in 3d oxides which can be written as follows

$$P_{O} = \sum_n \Pi_n (S_{O} \cdot S_{n})$$

where $S_{n}$ are the spins of the surrounding 3d ions, $\langle S_{O} \rangle \propto \sum_n \bar{I}_n S_{n}$ is a spin polarization of the oxygen ion due to the surrounding 3d ions with $\bar{I}_n$ being an exchange coupling tensor. It seems the oxygen exchange-induced electric polarization of purely electron origin has been too little appreciated in the current pictures of multiferroicity in 3d oxides.

4 Origin of multiferroic properties in the edge-shared CuO₂ chain compounds

4.1 Cancellation of the spin-dependent electric polarization in perfect edge-shared CuO₂ chains

Recent observations of a multiferroic behaviour concomitant the incommensurate spin spiral ordering in cuprates LiVCuO₄ [18,19,20] and LiCu₂O₂ [21] with nearly perfect edge-shared CuO₂ chains (see Fig. 1) challenge the multiferroic community. From the viewpoint of the spin-current model, these cuprates seem to be prototypical examples of the 1D spiral-magnetic ferroelectricities revealing the relativistic mechanism of "ferroelectricity caused by spin-currents" [13]. However, as we see from discussion above, isolated perfect edge-shared centrosymmetric CuO₂ chains cannot produce a spin-dependent electric polarization both of nonrelativistic and relativistic origin. Indeed, the net nonrelativistic polarization of a spin chain formed by Cu ions positioned at the center of symmetry can be written as follows [11]

$$P_{eff} = \Pi \sum_{j=even} \left[ (S_{j} \cdot S_{j+1}) - (S_{j} \cdot S_{j-1}) \right]$$

hence for a simple plane spiral ordering in perfect edge-shared CuO₂ chains we arrive at a twofold cancellation effect due to the zeroth value both of the $\Pi$ and the spin-correlation factor in brackets. A twofold cancellation effect takes place for the relativistic contribution [12] to the spin-dependent electric polarization as well, because both the exchange-dipole moment $\Pi$ and Dzyaloshinsky vector $D$ turn into zero. Indeed, a specific symmetry of Cu₁-O-Cu₂ bonds in edge-shared CuO₂ chains (see Fig. 1) results in a full cancellation of a net Dzyaloshinsky vector, though the partial Cu₁-O₁-II-Cu₂ contributions survive being of opposite signs [32,33].

The absence of a spin-dependent ferroelectric polarization in perfect edge-shared CuO₂ chains is a simple corollary of its centrosymmetry. The nonzero effect predicted by the spin-current model [13] is related to an unphysical symmetry breaking engendered by a strong fictive "external" nonuniform field needed to align spirally the chain spins. Thus we may state that the edge-shared CuO₂ plaquettes arrangement in the CuO₂ chains appears to be robust regarding the inducing of the spin-dependent electric polarization both of the nonrelativistic and relativistic origin. It means that we should look for the origin of puzzling multiferroicity observed in LiVCuO₄ and LiCu₂O₂ somewhere within the out-of-chain stuff.

4.2 Nonstoichiometry and multiferroic behaviour of edge-sharing CuO₂ chain compounds LiVCuO₄ and LiCu₂O₂

According to the spin-current theory [13] a net electric polarization induced by a spin-spiral ordering in CuO₂ chains of quantum helimagnets LiVCuO₄, NaCu₂O₂, LiCu₂O₂, and Li₂ZrCuO₄ with a very similar CuO₂ spin chain arrangement is directed as shown in Fig. 1 with a magnitude proportional to $\sin \phi$, where $\phi$ is the pitch angle. Thus we should anticipate comparable values of a net chain electric polarization in these cuprates with pitch angles 85°, 82°, 62°, 33°, respectively [83]. However, these cuprates show up a behavior which cannot be explained within the framework of spiral-magnetic ferroelectricity [13,14]. First, in accordance with a cancellation rule discussed above the quantum helimagnets NaCu₂O₂ and Li₂ZrCuO₄ do not reveal any signatures of a multiferroic behavior while the both LiVCuO₄ and LiCu₂O₂ systems reveal a mysterious behavior with conflicting results obtained by different groups. Indeed, Yasui et al. [19] claim that LiVCuO₄ reveals clear deviations from the predictions of spin-current models [14] while Schrettle et al. [20] assure of its applicability. In contrast to LiVCuO₄, LiCu₂O₂ shows up a behavior which is obviously counterintuitive within the framework of spiral-magnetic ferroelectricity [21] (see Fig. 2).
5 Electron-hole dimers, electronic phase separation, and dielectric anomalies in undoped parent manganites

Even the nominally pure globally centrosymmetric parent manganite LaMnO₃ exhibits a puzzling multiferroic-like behavior inconsistent with a simple picture of an A-type antiferromagnetic insulator (A-AFI) with a cooperative Jahn-Teller ordering. Its anomalous properties are assigned to charge transfer instabilities and competition between insulating A-AFI phase and metallic-like dynamically disproportionated phase formally separated by a first-order phase transition at $T_{\text{disp}} = T_{JT} \approx 750 \, \text{K}$ [23]. The unconventional high-temperature phase is addressed to be a specific electron-hole Bose liquid (EHBL) rather than a simple "chemically" disproportionated R(Mn²⁺Mn⁴⁺)O₃ phase. New phase does nucleate as a result of the charge transfer (CT) instability and evolves from the self-trapped CT excitons, or specific EH-dimers, which seem to be a precursor of both insulating and metallic-like ferromagnetic phases observed in manganites. The view of a self-trapped CT exciton to model a Mn²⁺-Mn⁴⁺ pair is typical for a chemical view of disproportionation, and is strongly oversimplified. Actually we deal with an EH-dimer to be a dynamically charge fluctuating system of coupled electron MnO⁶⁺⁻⁰ and hole MnO⁴⁻ centers having been glued in a lattice due to strong electron-lattice polarization effects. In other words, we should proceed with a rather complex physical view of disproportionation phenomena which first implies a charge exchange reaction

$$\text{Mn}^{2+} + \text{Mn}^{4+} \leftrightarrow \text{Mn}^{4+} + \text{Mn}^{2+},$$

(19)
governed by a two-particle charge transfer integral

$$t_B = \langle \text{Mn}^{2+}\text{Mn}^{4+}\rangle |\hat{H}_B|\langle \text{Mn}^{4+}\text{Mn}^{2+}\rangle,$$

(20)

where $\hat{H}_B$ is an effective two-particle (bosonic) transfer Hamiltonian, and we assume a parallel orientation of all the spins. As a result of this quantum process the bare ionic states with site-centred charge order and the same bare energy $E_0$ transform into two EH-dimer states with an indefinite valence and bond-centred charge-order

$$| \pm \rangle = \frac{1}{\sqrt{2}} (| \text{Mn}^{2+}\text{Mn}^{4+} \pm | \text{Mn}^{4+}\text{Mn}^{2+} \rangle )$$

(21)

with the energies $E_{\pm} = E_0 \pm t_B$. In other words, the exchange reaction restores the bare charge symmetry. In both $| \pm \rangle$ states the site manganese valence is indefinite with quantum fluctuations between +2 and +4, however, with a mean value of +3. Interestingly, in contrast with the ionic states, the EH-dimer states $| \pm \rangle$ have both a distinct electron-hole and inversion symmetry, even parity (s-type symmetry) for $|+\rangle$, and odd parity (p-type symmetry) for $|-\rangle$ states, respectively. Both states are coupled by a large electric-dipole matrix element:

$$\langle + | d | - \rangle = 2 e R_{\text{Mn-Mn}},$$

(22)
where $R_{\text{Mn-Mn}}$ is the Mn-Mn separation. In a nonrelativistic approximation the spin structure of the EH-dimer will be determined by the isotropic Heisenberg exchange coupling $V_{\text{ex}} = J \langle S_1 \cdot S_2 \rangle$, and the two-particle charge transfer characterized by a respective transfer integral which depend on the spin states. Both terms can be easily diagonalized in the net spin $S$ representation so that for the energy we arrive at

$$E_S = \frac{J}{2} S(S+1) - \frac{25}{2} \pm \frac{1}{20} S(S+1) t_B , \quad (23)$$

where $\pm$ corresponds to two quantum superpositions $|\pm\rangle$ with $s$- and $p$-type symmetry, respectively. It is worth noting that the bosonic double exchange contribution formally corresponds to a ferromagnetic exchange coupling with $J_B = -\frac{1}{10} |t_B|$. We see that the cumulative effect of the Heisenberg exchange and the bosonic double exchange results in a stabilization of the $S=4$ high-spin (ferromagnetic) state of the EH-dimer provided $|t_B| > 10J$ (see Fig.3) and the $S=1$ low-spin (ferrimagnetic) state otherwise. The spin states with intermediate $S$ values: $S=2$, 3 correspond to a classical noncollinear ordering.

The EH-dimer reveals unconventional magnetoelectric properties. Indeed, the two-particle bosonic transport and respective kinetic contribution to stabilization of the ferromagnetic order can be suppressed by a relatively small electric fields that makes the EH-dimer to be a promising magnetoelectric cell especially for the heavy rare-earth manganites RMnO$_3$ (R=Dy, Ho, Y, Er) with supposedly a ferro-antiferro instability. In addition, a strong anisotropy of the dimer's electric polarizability is noteworthy. In an external electric field the EH-dimers tend to align along the field.

Anomalous electric polarisability of the EH dimers and EH droplets that would result in dielectric anomalies in the EHBL phase and the phase-separated state of LaMnO$_3$. Indeed, such anomalies were reported recently both for poly- and single-crystalline samples of the parent LaMnO$_3$.[43,44] We have considered several mechanisms of spin-dependent electric polarization in 3d oxides. Starting with a generic three-site two-hole cluster and a realistic perturbation scheme we have deduced both nonrelativistic and relativistic contributions to the electric polarization. Nonrelativistic mechanism related to the redistribution of the local on-site charge density due to the $pd$ covalency and the exchange coupling is believed to govern the multiferroic behaviour in 3d oxides. The approach realized has much in common with the mechanism of the bond- and site-centered charge order competition (see, e.g. Ref.[45]) though we started with the elementary $pd$ charge transfer rather than the $dd$ charge transfer. An alternative approach to the derivation of the spin-dependent electric polarization was considered which is based on the parity-breaking exchange coupling and the exchange induced polarization. As an actual application of the microscopic approach we discuss recent observations of multiferroic behaviour concomitant the incommensurate spin spiral ordering in $s=1/2$ chain cuprates LiVCuO$_4$ and LiCu$_2$O$_2$. We argued that the multiferroicity observed in these nonstoichiometric cuprate samples has nothing to do with "spin currents" and can be consistently explained if one takes into account the nonrelativistic exchange-induced electric polarization on the Cu$^{2+}$ centers substituting for the positions native for the Cu$^{2+}$-ions in LiCu$_2$O$_2$ or the positions native for the Li$^+$-ions in LiVCuO$_4$, respectively. We argued that a charge transfer instability accompanied by nucleation of the electron-hole dimers and droplets in 3d oxides gives rise to a novel type of magnetoelectric coupling due to a field-induced redistribution of the electron-hole droplet volume fraction.

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