Ferroelectric current, electrospinons and ferrons in the underdoped copper oxides

Z. BAK*
Institute of Physics, Jan Dlugosz University of Czestochowa, 42-200 Czestochowa, al. Armii Krajowej 13/15, Poland

We study the magnetoelectric effects in the normal phase of the copper oxides. We show, that in the underdoped copper oxides there arises a peculiar, alternative to the magnon fractalization, mechanism of spinon excitations. Next we prove, that within the CuO_2 planes spinons are coupled to the local electric dipole moments which results in composed excitations called electrospinons. Further, we show that when external electric field is applied, along with the electric current there can also arise the ferroelectric current being the ferroelectric counterpart of the well-known spin current. Finally we show that magnetoelectric phenomena can contribute to the second harmonic generation.

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1. Introduction

The term *multiferroic* denotes the crystals in which several order parameters, ferroelectric, ferro-/antiferromagnetic, ferrotoroidic or ferroelastic are coexisting [1-4]. Mutual interplay between different multiferroic orderings is an inspiration for the search for new exotic matter states, excitations and the study of phase transitions. Major motivation to study multiferroic effects is a quest to find new perspectives of potential technological applications in the construction of electronic devices [5-6]. In our study special attention is paid to the magnetoelectric effects and other multiferroic effects in the copper oxides. We predict possibility of appearance of electric dipole current, a new transport phenomenon being electric counterpart of the spin current [7]. Anisotropy of the structure or magnetic interactions allows in this system a plethora of elementary excitations. Along with the conventional excitations like magnons or phonons there can arise both composed quasiparticles like electromagnons [3] or fractionalized like spinons [8]. In the quasi 1D anisotropic magnets spinons arise due to the fractalization of magnons. Below we are showing that in the mixed-valent oxides there exists peculiar mechanism which favours spinonic excitations. This explains why in the 124 underdoped copper oxides the density of the spinon states is much larger than the density of magnon-like excitations although 124 systems are quasi- 2D [9]. Further, we show that in some multiferroics there can arise a new type of composed excitations which we call *electrospinons* [10]. The electrospinons are formed of a charge carrier bound to a spinon and local electric dipole. Finally, we derive contribution of the specific to the copper oxides magnetoelectric effects, to the second harmonic generation.

2. Magnetoelastic interactions within the CuO_2 plane

We focus our attention on the underdoped copper oxides. The most interesting physics of these systems is associated with the CuO_2 planes. As we know in an ideal tetrahedral symmetry it is expected that Cu 3d and O 2p orbitals point directly toward each other and produce strong covalent bond. Moreover, it is expected that localized Cu^{+2} spins can be well described by the 2D Heisenberg Hamiltonian, and a weak coupling between the $Cu0_2$ layers leads to the formation of a three-dimensional Neel-ordered state. This is true as long as the elastic effects are neglected. The in-plane stress causes (the magnetovolume effect) the Cu-O-Cu bonds to be bent from 180^o degree by displacing away from Cu-0 plane the oxygen ions. This can be realized either by the tilt of the CuO_6 octahedra (in the 123 systems see Fig. 1) or bond buckling (see Fig. 2) [11].The buckling causes relative shift (the parameter b indicated in fig 2) of positive Cu^{+2} and negative O^{-2} ions and makes that each Cu-O-Cu bond carry an ancillary electric polarization P. The rough estimation of the associated to each bond electric dipole moment is P= **2e b.** As the induced dipoles are parallel there arises the ferroelectric order as observed in some copper oxides [13]. Coexistence of antiferromagnetism and ferroelectricity means that we have multiferroic order. According to the Kanamori rule the Cu-O-Cu bond buckling reduces the exchange integrals and in consequence there arise magnetoelastic and magnetoelectric interactions [1].

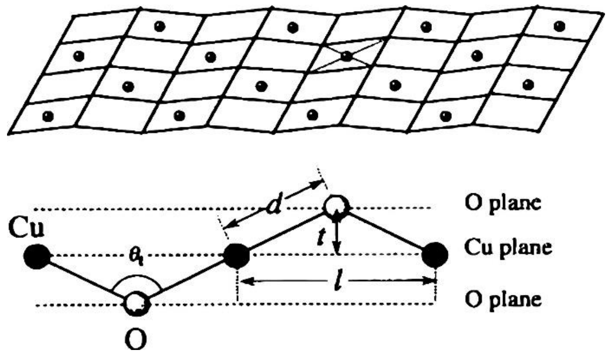

Fig. 1. CuO_2 plane modification due to the tilt of the CuO_6 octahedra [11]

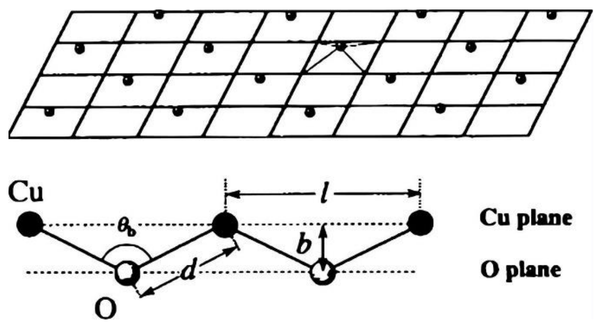

Fig. 2. CuO_2 plane modification due to the buckling of the Cu-O-Cu bonds [11].

Buckling parameter bin the 123 can achieve 0.28 A compared to the 1.94 A Cu-O bond length [11-12]. Buckling or tilting causes that the antiferromagnetic order becomes non-collinear. This can be modelled by the Dzialoshinsky-Moriya /DM/ interaction. When magnetic and electric orders coexist simultaneously there arises their mutual coupling resulting in a wide range of magnetoelectric phenomena. This makes magnetic excitations electrically dipole active and gives rise to combined elementary excitations called electromagnons.

3. Hole doped copper oxides

Copper oxides with stoichiometric composition are less interesting from both fundamental and technological point of view. The situation changes upon doping. As the CuO_2 plane is more sensitive to hole doping we focus our attention on this case. Introduction of nonisovalent dopants distorts charge distribution and the charge neutrality is recovered by the appearance of extra holes. Additional holes go to the CuO_2 plane and as the rule localize at 2p oxygen orbitals. Hole doping into the CuO_2 plane removes electrons from Cu-O bonds and as the in-plane Cu-O bonds are of antibonding character, hole doping strengthens them. Therefore, hole doping leads to shortening of the (in-plane) Cu^{+2}-O^{-1} bond. As the consequence the initially buckled bonds in the Cu^{+2}-O^{-2}-Cu^{+2} configuration in the Cu^{+2}-O^{-1}-Cu^{+2} state become flattened (no buckling). As the result there is no electric dipole associated to the hole doped Cu^{+2}-O^{-1} bond. There is another effect associated with the flattening of the Cu-O-Cu bond.

The Dzialoshinsky-Moriya spin interaction present in the considered system has the form

$$H = \sum_{ij} d_{ij} S_i \times S_j \qquad (1)$$

The DM vector $\mathbf{D_{ij}}$ for two magnetic ions coupled by the exchange mechanism via intermediate oxygen ion is given by [14]

$$D_{ij} \sim \left| r_i \times r_j \right| \qquad (2)$$

where $\mathbf{r_i}$ and $\mathbf{r_j}$ are oriented along the neighbouring Cu-0 bonds. Collinearity of the Cu-O bonds means that in the case of intervening O^{-1} oxygen ion the DM interaction between two neighbouring, in-plane spins is switched off. Mixed valent behaviour of the oxygen (O^{-2} to O^{-1} conversion) modifies magnetic coupling of the spins centred on the neighbouring Cu^{+2} ions. The spin coupling in the Cu^{+2} –O^{-2}-Cu^{+2} configuration is the well-known superexchange that favours antiferromagnetic ordering of spins along chain. Contrary to the former case the spin coupling via the Cu^{+2} - O^{-1}- Cu^{+2} exchange path (electron exchange across O^{-1} instead of O^{-2} ions) is the double exchange which favours ferromagnetic ordering of neighbouring Cu^{+2} spins. As the consequence along the bond direction the local parallel ↑↓↑↑↓↑ ordering of spins is to be expected, which is nothing but the localized spinon [15]. This explains why in the hole doped copper oxides the spinon excitations dominate the magnon ones [9]. Properties of the spinon excitations are discussed in the next chapter. Independently, conventional mechanisms of magnon and spinon creation are still active. Spinon carries spin S=1/2, which couples to the S=1/2 spin of the hole and effectively the bosonic *holon* [16] quasiparticle is created. Below we are showing that this holon is dressed by an electric dipole moment which creates a new transport phenomenon.

Homogenous distribution of holes can realize only for low concentration of the hole doping. Shortening of the Cu^{+2}-O^{-1} bond due to the misfit strain [17] interaction attracts other hole to the parallel bond in the neighbouring chain within the CuO_2 plane. At higher hole concentration the misfit strain is relaxed, dislocation relaxes tensions and this generates separation of hole rich and hole depleted region called nanostripes [18].

At higher hole concentration there arises phase separation onto the hole rich and hole depleted regions organized in a nanostripe 1D structures. In the hole rich regions with short bonds and no multiferroic order the onset of superconductivity is favoured. The buckled bond regions multiferroic order act against it. The boundary between both regions is not necessarily sharp. In the case when charge neutrality is induced by the introduction of interstitial dopants there can arise more complicated structures.

In the 124 and other cuprates the scanning x-ray diffraction, with focused synchrotron radiation, shows existence of fractal structures in the proximity of the stripe critical point [12]. The x-ray diffraction of the copper oxides shows in addition to the main peak some satellite reflection peaks produced by ordering of oxygen interstitials /O-i/. The satellite peaks are associated with a non-uniform (fractal) distribution of the O-i dopants. The probability distribution of the oxygen dopants can be quantified by the power law $P(x) = x^{\alpha} \exp(-x/x_o)$ [19-20]. The experimental data can be fitted with power law exponent $\alpha = 2.6 \pm 0.2$. This is the direct evidence of the fractal structure. Moreover, the experimental data show that high temperature SC is favoured by the appearance of the fractal structure. This may suggest that elementary excitations can have fracton magnon or fracton spinon structure. [20-21]

4. Spinons

Low dimensional or highly anisotropic magnetic materials possess exotic ground-state properties such as resonating valence bond /RVB/ quantum states. In such systems one can observe a variety of excitations absent in bulk materials. Their statistics and quantum numbers, can be exotic and different from those of the constituent particles. One well-known example is discussed below. In isotropic ferromagnets and antiferromagnets /AFM/ the elementary excitations are always the S =1 spin-flip magnons, and the spectrum exhibits a sharp, single-magnon mode [22]. However, in strongly anisotropic systems in which the magnetic interaction in one direction dominates over the two others the lowest excitations are the spinons [15]. In such systems (chain-like ones) a spin-flip splits and creates two elementary S=1/2 excitations — called spinons. Each spinon carries S=1/2 and no charge. Such a phenomenon of carrying only a fraction of the quantum numbers is called fractionalization [23]. In general in anisotropic AFMs magnons and spinon excitations coexist with different excitation spectra. In the S=1/2 antiferromagnet, one would expect elementary excitations in the form of spin waves with the spectrum given by:

$$\omega_{mgn} = 2J\,|\sin(ka)|\,. \tag{3}$$

Contrary to this the spectrum of spinons is given by [8]

$$\omega_{sp} = \pi J/2\,|\sin(ka)|. \tag{4}$$

5. Electrospinons

As the multiferroics, like discussed above, show coexistence of several order parameters it is interesting to study their mutual interplay and its potential applications. Therefore it is necessary to study the fundamental interactions between the electric, elastic and magnetic states of the material. Especially, if magnetoelectric and/or magnetoelastic couplings are relatively strong. For potential applications of such materials it is important to know specific features of transport phenomena. Usually in solids, charge, spin or heat transport is mediated by a separate flow of respective (electron, magnon or phonon) carriers. In multiferroics there is significant role of composed quasiparticles which moving simultaneously contribute to more than one (charge, spin or heat) current. Recently much attention has been drawn to the electromagnon, a composed quasiparticle that involves magnetic and electric polarizations. Till now, there is no detailed study of composed quasiparticles which involve spinons.

The applied external field in the direction perpendicular to the CuO_2 plane can create induced electric dipole. This will affect (damp) the spinon excitation as we have shown above. Thus we can see that we have strong electro-magnetic interaction in the system. Strong electro-magnetic coupling is the source of new composed excitations called *electromagnons.* [3]. Strong spin-lattice coupling dresses also the spinons and promotes excitation of fractionalized counterparts of electromagnons which we call *electrospinons}* [24]. This dressing enables the electric-field control of magnetic excitations coupled to electric dipoles. There is no experimental technics which give evidences of electromagnons or electrospinons directly. The efficient method which gives indirect evidence of strong spin-lattice coupling leading to the spin-phonon excitation is the study of magnetic contribution to the heat conduction [25]. As we have shown before the extra hole located at the oxygen site of the Cu-O-Cu bond removes bond buckling and consequently annihilates the local electric dipole. This effect can be interpreter as if an opposite (to the background of local dipoles) electric dipole is bound to the holon, such a composite excitation we call *ferrons.*

6. Ferroelectric current

The inhomogeneous (partially localized) distribution of the excitation does not preclude quasiparticle hopping as required for the onset of SC. Under some conditions the hole become mobile and in the normal state external applied voltage results in holon hopping which creates an electric current. As we have shown above, contrary to the others the bond which involves O^{-2} oxygen (i.e. occupied by the holon) is flattened. This means that the local electric dipole at this bond vanishes. It has been shown that exchange across the O^{-1} (extra hole) intervening oxygen ion produces alternative (small) contribution to the local electric polarization given by [24].

$$P = -I\,\frac{eV}{3\Delta}\,\frac{e_{12}\times e_1\times e_2}{\left|\cos(\theta_{12}/2)\right|} \tag{5}$$

where $\mathbf{e}_{12}$ is the unit vector parallel to the direction of the bond from site M1 to site M2, and θ_{12} is the angle between the two magnetic moments $\mathbf{M1}\cdot\mathbf{M2} = M^2\cos\,\theta_{12}$, while $\mathbf{e_i} = \mathbf{M_i}/|M_i|$. When holon jumps to the neighbouring oxygen site in its former position both buckling as well as electric dipole is restored. Simultaneously at the new location the value of an electric dipole is lowered. For the electric dipole this process is equivalent to the shift in the opposite direction to the holon jump. This means that electric current is accompanied by the counter flow of electric dipole current. This effect we call the *ferroelectric current* that is carried by the ferrons. Such phenomenon is the electric counterpart of the spin current. This is novel, very peculiar phenomenon since in conventional ferroelectrics the electric dipoles arise due to the relative positive and negative ion shift thus electric dipoles are always immobile.

7. Magnetoelectric effect and second harmonic generation

To complete review of magnetoelectric phenomena let us discuss the possibility of the second harmonic generation /SHG/ in the copper oxides. In some materials two photons with the same frequency via nonlinear process can generate new photons with twice the energy, and therefore twice the frequency of the initial photons. Second harmonic generation, as an even-order nonlinear optical effect, is only allowed in media without inversion symmetry [26].

In the multiferroics there exists coupling of magnons with a macroscopic electric polarization **P**, which in turn is coupled either by the Dzialoshinsky-Moriya /DM/ interaction $\mathbf{V} \sim S \times S_j$ or by the exchange strict ion mechanism. The additional electrical polarization (in the case of electrostrictive /ES/ mechanism being active in the system) is associated with the variation of the scalar exchange field $\delta P \propto \Delta(S_i \cdot S_j)$. Usually only the first order perturbation is considered, however it is interesting to go a step further. Up to the second order perturbation the variation of the exchange field is given by

$$\Delta(S_i \cdot S_j) \approx S_i \cdot \delta S_j + \delta S_i \cdot S_j + \delta S_i \cdot \delta S_j \qquad (6)$$

Provided that the perturbation is associated with an incident light beam of frequency ω the v variations of local magnetic moments behave as $\delta S_i \sim S_i - \cos(\omega t)$. When the ES magnetoelectric coupling is active the additional polarization that arises due to the perturbation the third term of the expansion in Eq. (6) generates the SHG effect. SHG effect is absent in the centrosymmetric crystals, however, as we can see from above in the case under consideration such a condition is not the prerequisite. There is no contradiction since in our case the perturbation breaks the symmetry locally thus total asymmetry is not necessary to SHG effect. We should point out here that the DM interaction gives no contribution to the SHG effect as contrary to the ES mechanism the second order perturbation term $\delta S_i \times \delta S_j$ equals zero.

When the electric field is applied in the direction perpendicular to the CuO_2 plane one would expect relative shift of the Cu^{+2} and O^{-2} ions. This changes the buckling angle as well as the interionic separation. With the change of the Cu-O-Cu bonds angle according to the Kenmore rule the respective exchange integral is changed. This means that magnetoelectric effect is possible due to the dependence of coupling parameters J_{ig} on their separation which in turn can be modulated by the external field according to the formula.

$$J_{ij} = J_{ij}^0 + (\partial J_{ij} / \partial u)(\partial u / \partial E)E \qquad (7)$$

Where J_{ir}^{o} is the exchange integral for the unperturbed crystal, while u denotes the relative change of displacement. Within the Lorenza model of the dielectric constant €(ω) for the electric dipole or magnetic permeability μ(ω) the transmission spectra reads

$$\mu(\omega) = 1 + \sum_j \frac{S_j}{\omega_j^2 - \omega^2 - i\omega\gamma_j} \qquad (8)$$

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{S_j}{\omega_j^2 - \omega^2 - i\omega\gamma_j} \qquad (9)$$

where ε_∞ is the high frequency dielectric constant, ω_j and Υ_j denotes the resonant frequencies and the damping rates respectively, while S_j is the respective spectral weight. One would expect that magnetoelectric coupling shows maxima around the resonant frequencies when electronic structure is reorganized which in turn affects the exchange integrals and orientation of the magnetic moment. The DM mechanism for dipole creation $\delta P \propto \Delta(S_i \cdot S_j)$ is effective in the case of frustrated or spiral spin structures. Contrary to this ES can be effective in the case of collinear AFM. In this case it is possible formation of spinons. Both effects coupled can give rise to a new type of quasiparticles called electrospinons.

8. Discussion and summary

With the rapid miniaturization and increase of operational speed of microelectronic devices, a great amount of redundant heat is produced, which will in turn affect device performance [26]. In the underdoped cuprates the conventional models of phonon heat transport based on phonon-defect scattering or conventional phonon-electron scattering fail to explain the experimental data [xxx]. On the contrary there are experimental evidences for a sizable magnetic contribution to the zero field heat transport [27] .Thus the heat dissipation and transport by other e.g. magnetic mechanism is becoming more and more important. The ballistic flow of electrospinon ferron excitations might add an additional contribution $\Delta J = \kappa_{mag} \nabla T$ to the diffusive heat current **J** or they scatter with phonons and therefore suppress the phonon heat transport. We believe that electrospinon/ferron currents can rival or even exceed heat transport generated by other quasiparticles and can be manipulated from outside by the electric field. This opens a new field of application being the analogue of the spin caloritronics [28-29].

Our study concentrates on the physics of non-superconducting phase of copper oxides. However, one of the fundamental questions of contemporary condensed matter physics is devoted to the quest of pairing interaction in high-temperature superconductors. We point to important role of the magnetic fluctuations supported by the elastic and magnetoelectric interactions. We argue for the idea that a few pairing mechanisms contribute to superconductivity. It has been shown that cooperation of two pairing mechanisms can give rise to T_c five times higher than those arising from any of these mechanisms acting alone [xx]. As the RVB theory by Anderson [xx] takes the spin-charge separation as the starting point of the theory the RVB is qualitatively consistent with our approach. Thus RVB is possibly one of the mechanisms which contribute to the onset of superconductivity in the copper oxides. We point to another hint indicating for the important role of the magnetic interactions in the onset of superconductivity. The spectrum of magnons and spinons is linear in the wave-vector **k** and as it was shown in [30-31] its thermodynamical behaviour is governed by the spectral dimension $\alpha = 4$, which facilitates condensation of pre-existing Cooper pairs.

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* Corresponding author: z.bak@ajd.czest.pl