Out-of-plane ionicity *versus* in-plane covalency interplay in high- T_c cuprates

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It may be argued that the remarkable properties of the high-temperature superconducting cuprates such as the insulator–metal transition (IMT) and the metal–superconductor transition (MST) originate from competition and interplay between the interlayer ionic interaction and the intralayer covalent bonds in these materials. It is proposed here that the microscopic order parameter is the local field estimated from the ionic polarization at the sub-unit cell level, and it is demonstrated that it shows a strong temperature as well as chemical doping dependence. The out-of-plane ionicity induces an interlayer electron transfer that reduces the ionicity of the layers and leads to IMT, while the in-plane covalency induces in-plane intersite hole transfer that increases the out-of-plane ionicity. It is suggested that this competition leads to a local field catastrophe at a critical temperature T_c that drives the compound to MST. The asymmetry of the free charge carrier density breaks locally the mirror reflection symmetry of the order parameter, leading to a pairing between the real current and the polarization current.

1. Introduction

The ionic model has provided the basis for our understanding of the very wide range of physical phenomena displayed by ionic crystals (Mott & Gurney, 1946; Cox, 1992). However, peculiar electrical and structural behaviours of some ionic crystals known to display large values of a spontaneous polarization result from an unusual feature of the ionic *versus* covalent nature of bonds (Cohen, 1992). In the ABO_3 type of ferroelectric perovskite crystals, a mixed ionic–covalent $B–O$ bond is a necessary condition for the occurrence of a spontaneous polarization in this type of material (Cohen & Krakauer, 1992).

In general, the chemical bond in ferroelectric perovskites should be considered, more or less, as a transition state between the ionic and the covalent one. The simplest, but most general, method of estimation of ionicity comes from the theory of electronegativity. The ionic character of the bond can be quantified by the charge transfer which is a function of electronegativity difference between the cation and anion in the lattice. The ionicity obtained in this way has a simple physical meaning: it is the charge transferred between two atoms during the formation of the bond and is referred to as the maximal charge determined in relation to the pure ionic structure. This means that, in the perovskites, the valence electrons are partially transferred back from the anions to the cations as the covalent bond forms. An interplay of the covalent and the ionic interaction takes place (Tkacz-Smiech *et al.*, 2000).

In titanates, such as $BaTiO_3$, all calculations reveal that the charge transfer from Ti to O is not complete. If $BaTiO_3$ was

purely an ionic crystal the 3*d* and 4*s* electrons of Ti would be entirely transferred to oxygen, yielding a nominal charge of +4 for Ti. However, because of the partial hybridization between O 2*p* and Ti 3*d* states, these electrons remain partly delocalized on the Ti atom, so that the static charges on the Ti and O atoms are smaller than they would be in a purely ionic material (Ghosez *et al.*, 1998). If the Ti–O bond is strained and Ti moves closer to O, ionic polarization is produced. But, at the same time, the *p*–*d* hybridization is increased, and an electron is virtually transferred from O to Ti which produces a virtual current from Ti to O. It is now possible to calculate polarization using the Berry phase method from single-electron wavefunctions (King-Smith & Vanderbilt, 1993; Resta, 1994).

The high-temperature superconductor (HTSC) cuprates are ionic perovskite crystals with a charge transfer insulator parent compound (Zaanen *et al.*, 1985). In fact, the crystal structure of all cuprate high-*T_c* superconductors can be considered as stacks of alternating anionic CuO₂ layers and block layers which are mostly cationic. The stacking direction is commonly taken as the crystallographic *c* direction. However, the CuO₂ layer which is shared by all cuprate superconductors demonstrates a strong in-plane covalent bonding between Cu 3*d_{x²−y²}* orbitals and O *p_{xy}* orbitals.

Many physical properties, such as resistivity and the critical temperature *T_c*, are strongly dependent on the density of charge carriers in the anionic CuO₂ plane which is regulated by variation of the cationic block layer composition. However, the maximum *T_c* varies widely between crystals sharing the same basic CuO₂ in-plane electronic structure, by up to a factor of 10 at the same hole density in monolayer cuprates (Eisaki *et al.*, 2004). These variations, as mentioned by Ohta *et*

al. (1991) and Slezak *et al.* (2008), cannot be due to the doping dependence of the CuO₂ in-plane electronic structure, and it has been assumed for a long time that there must be a key out-of-plane influence that controls the basic electronic structure of cuprates (Eisaki *et al.*, 2004).

Moreover, angle-resolved photoemission spectroscopy (ARPES) (Lanzara *et al.*, 2001) and X-ray absorption spectroscopy (XAS) have revealed a local displacement of oxygen as carriers are doped (Bianconi *et al.*, 1996), indicating an intimate relation between the lattice effects and the pairing mechanism. Also, isotope and strain (pressure) effects are considered as direct experiments that establish the role of the lattice in the HTSC (Khasanov *et al.*, 2004).

In this paper, it is shown that the microscopic order parameter (OP) which is responsible for the physics of high-*T_c* superconductors (Guerfi, 2011, 2013), especially the IMT (insulator–metal transition) and the MST (metal–superconductor transition), is the local field that reflects interlayer polarization. Through a competition between the interlayer ionic interaction and the intralayer covalent nature of bonds (mainly in the CuO₂ plane in the cuprates case), this OP shows a strong chemical as well as temperature dependence. The paper is organized as follows. In §2 we give a definition of the microscopic OP. In §3 we study the chemical dependence of the OP and establish its direct connection with the IMT. In §4 we focus on the temperature dependence of the OP and we suggest that the competition between the interlayer ionic interaction and the intralayer covalent nature of bonds drives the compound to MST.

2. The microscopic order parameter

HTSCs are ionic crystals with a charge transfer insulator parent compound. The O *p* level and the Cu *d* level form hybridized bonding and anti-bonding orbital states, and the gap lies between the filled *p*-like O band and the empty Cu *d*-like band (Egami, 2002). In the purely ionic model for cuprate compounds, nominal valence charges are taken in order to compute the ionic polarization at the sub-unit-cell level (the OP) in these materials. It is noted that these materials are centrosymmetric; thus, the total ionic polarization at the unit-cell level vanishes at any given temperature and there would be no external electric effects. However, the local field which acts on a particular atom (layers) is influenced by the nearest surroundings and therefore can deviate from the average field.

The microscopic OP, which is the local field that reflects interlayer polarization, is estimated from the ionic polarization at the sub-unit-cell level and is given by

$$P = \frac{1}{\Omega} \sum q_i r_i = \text{order parameter.} \quad (1)$$

Ω is the unit-cell volume, q_i are the nominal ionic charges located at the atomic positions r_i . Fig. 1 shows the crystal layered structure of YBa₂Cu₃O₆ and YBa₂Cu₃O_{7−δ} considered as a juxtaposition along the *z* axis of successive layers including the anionic CuO₂ layer which is characterized by strong in-plane hybridization (covalent bonding). One can

Figure 1

Crystal structure of YBa₂Cu₃O₆ and YBa₂Cu₃O_{7−δ} considered as a juxtaposition along the *z* axis of successive layers including the anionic CuO₂ layer which is characterized by strong in-plane hybridization (covalent bonding). One can switch from the insulator compound to the superconductor one by chemical doping. Because of charge redistribution, upon doping, the sign of the OP is inverted compared with the parent undoped case. The mirror plane *M*, which is the yttrium plane, divides the unit cell into two sub-unit cells.

switch from the insulator compound to the superconductor one by chemical doping which is achieved in most cases by adding oxygen to the parent insulator compound. Because of charge redistribution, upon doping, the sign of the OP is inverted in $\text{YBa}_2\text{Cu}_3\text{O}_7$ compared with the parent undoped $\text{YBa}_2\text{Cu}_3\text{O}_6$ compound. This is a consequence of the ionicity which induces a local redistribution of charges inside the compound as oxygen is added.

Fig. 2 illustrates the z coordinate of the centre of cations G^+ and the centre of anions G^- along with the z coordinate of anions and cations in the sub-unit cell, for the undoped $\text{YBa}_2\text{Cu}_3\text{O}_6$ and the doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$. The order of centres is inverted in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compared with the parent undoped $\text{YBa}_2\text{Cu}_3\text{O}_6$ case. However the G^+ and the G^- lie between the CuO_2 layer and the BaO layer in both compounds which means these layers are the first nearest neighbours that are influenced by the modification of the local field.

3. Chemical doping dependence of the microscopic OP in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

The influence of oxygen doping on normal and superconducting states of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxide has been extensively studied (Jorgensen *et al.*, 1990). Experimentally, it was found that in the range of oxygen content $6.35 \leq 7 - \delta \leq 7.0$ this compound has an orthorhombic crystal structure with a normal metallic state and a superconducting state at a critical temperature that decreases as the oxygen content decreases (Jorgensen *et al.*, 1990). At an oxygen content corresponding to $7 - \delta = 6.35$, superconductivity disappears and the oxide $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$ undergoes a simultaneous IMT and an orthorhombic-to-tetragonal structural phase transition (Jorgensen *et al.*, 1990). For an oxygen content $6.0 \leq 7 - \delta \leq 6.35$, the material remains an insulator in the tetragonal phase.

Figure 2
Chemical doping changes the sign of the OP. The redistribution of charges due to the ionic bond formation modifies the local field between the CuO_2 anionic layer and the adjacent layer. Coordinates of the centre of cations G^+ and anions G^- in the sub-unit cell exchange from the undoped $\text{YBa}_2\text{Cu}_3\text{O}_6$ to the doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$.

The nominal valence charges q_i that have been assigned for the different constituent ions are +3 for Y, +2 for Ba, -2 for O and a nominal charge for Cu balancing exactly the negative total valence charge of the oxygen. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, the nominal valence charge that has been assigned for copper is +2.2667. The positions r_i of the ions inside the sub-unit cell have been chosen on the basis of high-resolution neutron diffraction crystallographic data (Jorgensen *et al.*, 1990; Cava *et al.*, 1990). Fig. 3 illustrates the oxygen content dependence of the OP, estimated from the ionic polarization computed in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at 300 and 5 K, respectively. The OP $P(7-\delta)$ shows almost a linear behaviour for all oxygen content; however, it vanishes for oxygen content corresponding to $7 - \delta = 6.35$ and its sign is inverted for the $6.35 \leq 7 - \delta \leq 7.0$ oxygen content range compared with its sign in the $6.0 \leq 7 - \delta \leq 6.35$ oxygen content range. The highest value of the OP corresponds to optimally oxygenated samples.

The oxygen dependence of the OP (the local ionic polarization field) is consistent with the oxygen dependence of the physical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. It is noteworthy that $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ undergoes an IMT and superconductivity disappears at oxygen content $7 - \delta = 6.35$, while the OP vanishes at the same oxygen content; this suggests a direct link between the OP and the observed IMT.

As the oxide is doped with oxygen, ionicity induces charge redistribution inside the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ material which in turn modifies the local field. The important effect of this modification is to tilt all the bands; however, mainly because of the strong in-plane covalent character of bonds of the CuO_2 layer, the amplitudes of the static charges of the corresponding ions are reduced. The bands that correspond to the cationic layer are lowered relative to those of the anionic CuO_2 layer and to those of the CuO layer (the band of this layer is influenced by the local field as second nearest neighbour) compared with the

Figure 3
Oxygen content dependence of the OP (the ionic sub-unit cell polarization) in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The figure shows the OP at 300 and 5 K. It is noteworthy that while the microscopic OP vanishes for $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$ ($\delta = 0.65$), the oxide $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$ undergoes an IMT at the same oxygen content. This suggests a strong link between the OP and the IMT observed in the oxide.

parent undoped case of $\text{YBa}_2\text{Cu}_3\text{O}_6$, causing a possible arrangement of the electronic structure that consists of an interlayer transfer of electrons from the adjacent layers CuO_2 and CuO towards the BaO layer. Fig. 4 illustrates this interlayer electron transfer. This mechanism reduces the interlayer ionicity (along the z axis) and cancels the resulting local electric field driving a hole doping of the p -like band of O of both the plane and the chain. However, hole charges are mainly located on the CuO_2 layer as supported by experiments. It is noteworthy that a similar mechanism involving charge transfer of electrons stabilizing the structure of polar oxide surfaces has also been observed to lead to a two-dimensional metallic surface state (Wander *et al.*, 2001). Accordingly, in the range of oxygen content $6.35 \leq 7 - \delta \leq 7.0$ the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxide shows a metallic behaviour. At oxygen content $7 - \delta = 6.35$ the OP vanishes and the

Figure 4

Interlayer transfer of electrons, in YBCO oxide, from the anionic layer CuO_2 and CuO layer to the adjacent cationic layer BaO reduces the ionicity of the layers and removes the OP (local field) which otherwise will be present.

Figure 5

Bond-length changes along the c axis, as a function of oxygen doping, of $\text{Ba}-\text{O}_4$ and $\text{Cu}_2-\text{O}_{2,3}$. Ba and O_4 of the cationic layer approach each other when an IMT cancels the resulting local field; however, Cu_2 and $\text{O}_{2,3}$ of the anionic layer do not experience the field much as no significant bond-length variation along the c axis is observed; the strong in-plane covalent character of the bonds reduces significantly the amplitude of the static charges.

compound undergoes an IMT and the material remains an insulator for oxygen content $6.0 \leq 7 - \delta \leq 6.35$.

In Fig. 5 we plot the bond-length variations along the c axis as a function of oxygen content in the oxide of $\text{Ba}-\text{O}_4$ and $\text{Cu}_2-\text{O}_{2,3}$. The apical oxygen O_4 and the Ba ions move in opposite directions (approaching each other) along the z axis relative to the parent undoped case. The apical oxygen O_4 tends to approach the anionic CuO_2 layer, conversely to Ba. Mainly because of the strong in-plane covalency, the copper Cu_2 and the oxygen $\text{O}_{2,3}$ do not experience the field much as no significant displacements are observed.

4. Temperature dependence of the microscopic OP in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$

Assuming always nominal valence charges for the different constituent ions of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$, the atomic positions for different temperatures are taken from the crystallographic data (Schäfer *et al.*, 1988). Fig. 6 illustrates the temperature dependence of the OP (the local ionic polarization field) in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$. The compound $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ exhibits a local ionic polarization of 0.1959 C m^{-2} along the c axis (the polar axis) at 300 K and 0.2100 C m^{-2} at 92 K which is the superconducting transition temperature. The main feature of this plot is a step-like increase in the superconducting transition temperature of the OP which can be considered as a local ionic polarization catastrophe that occurs simultaneously at the critical temperature T_c .

It is noteworthy that at $T = 5 \text{ K}$ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is in superconducting state for almost the whole range of oxygen doping greater than 6.35. In this range, the values of the OP should differ from those at $T = 300 \text{ K}$. A linear fit of the plots of the OP at 300 and 5 K is given in Figs. 7 and 8, respectively. We have found a value of the slope equal to 0.39 for $T = 300 \text{ K}$; however, its value is found to be equal to 0.42 for $T = 5 \text{ K}$. This variation of the slope means that there is a 7.69% increase in the OP relative to its value in the normal state in the whole range of oxygen content greater than 6.35. This result is in excellent agreement and very consistent with what is

Figure 6

Temperature dependence of the OP in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$. A step-like increase of the OP is observed at the critical temperature considered as an ionic polarization catastrophe which results from the competition between the out-of-plane ionicity and the in-plane covalency in the oxide.

presented in Fig. 6 where the transition to the superconducting state of $\text{YBa}_2\text{Cu}_3\text{O}_{6.90}$ is accompanied by a change in the OP of 7.53% in superconducting state relative to the normal state (300 K).

The Born effective charge is a tensor Z_{ij}^* , which relates the change of polarization ΔP_i with the displacement u_j for a given volume of cell V_{cell} as

$$\Delta P_i = \frac{Z_{ij}^* e u_j}{V_{\text{cell}}} \quad (2)$$

This effective charge is enhanced in ferroelectric oxides by a strong orbital hybridization as compared with the nominal valence state of ions. In these ferroelectric oxides, covalency induces an electronic polarization that points in the same direction as the ionic polarization, doubling the Born effective charge in many cases (King-Smith & Vanderbilt, 1993; Resta, 1994). However, in cuprate materials, the in-plane displace-

Figure 7
Oxygen content dependence of the OP at 300 K. A linear fit gives a value of the slope of 0.39.

Figure 8
Oxygen content dependence of the OP at 5 K. A linear fit gives a value of the slope of 0.42.

ment of Cu^{2+} towards the oxygen $\text{O}_{2,3}$ induces an in-plane hole transfer (instead of electron transfer in the case of ferroelectric oxides) from the p -like band of oxygen to the d -like band of copper as was pointed out by Egami (2002). Fig. 9 illustrates this inter-site hole transfer. In fact, there is a large volume of literature that shows coupling of superconductivity to the lattice and phonon (Lanzara *et al.*, 2001; Pintschovius & Reichardt, 1994; Egami & Billinge, 1996; Mook & Doğan, 1999). In particular, the in-plane $\text{Cu}-\text{O}$ longitudinal optical (LO) bond-stretching phonon mode was observed by neutron inelastic scattering to show a strong softening with doping near the zone boundary along the $\text{Cu}-\text{O}$ bond direction (Pintschovius & Reichardt, 1994; Pintschovius *et al.*, 1991; McQueeney *et al.*, 1999). Also the LO phonon dispersion observed by inelastic neutron scattering measurements on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) suggests that the frequencies of the LO phonons are strongly softened with doping near the zone boundary (Egami *et al.*, 1999). This mode induces charge transfer between Cu and O, and thus couples strongly to the charge (Egami & Billinge, 1996; Ishihara *et al.*, 1997; Petrov & Egami, 1998). Although the in-plane electronic polarization points in the opposite direction to the ionic polarization, the hole transfer increases the amplitude of the static charge of both copper and oxygen, increasing the out-of-plane ionicity

Figure 9
The displacement of Cu^{2+} towards the oxygen $\text{O}_{2,3}$ induces an in-plane hole transfer (instead of electron transfer in ferroelectric oxides) from the p -like band of oxygen to the d -like band of copper. The in-plane ionic polarization is antiparallel to the in-plane electronic polarization; however, this hole transfer increases the out-of-plane electronegativity difference which in turn induces an out-of plane electron transfer causing the vanishing OP to re-emerge.

in the compound which in turn induces electron transfer from the plane to the chain. This behavior can be explained if one considers the scale of electronegativity based on the force of attraction (F) between the nucleus and the electron from a bonded atom, as first proposed by Allred & Rochow (1958):

$$F = \frac{e^2 Z_{\text{eff}}}{r^2}, \quad (3)$$

where e is the charge of the electron and r is the distance between the electron and the nucleus. (The electron is considered to be at the covalent boundary, r , of the atom.) Z_{eff} is the effective nuclear charge (less than the actual nuclear charge due to screening).

The force of attraction given by equation (3) is an approximate measure of the extent to which an atom in a molecule attracts electrons to itself, and therefore a measure of what might be called the absolute electronegativity of an atom (Allred & Rochow, 1958).

However, in the case of cuprates, when holes are transferred to copper, the charge of the electron has to be replaced by its effective charge e^* which is less than the actual charge e due to the screening by holes so that the absolute electronegativity of the copper decreases. This in turn increases the out-of-plane electronegativity difference and induces electron transfer from the plane to the chain.

Because of this additional out-of-plane electron transfer, the vanishing local polarization field (the OP) will re-emerge again and holes from the chain layer are partially removed. However, the apical oxygen plane will be tilted again, causing hole doping of the p band of the in-plane oxygen. This last conclusion is in good agreement with the experimental result of Magnuson *et al.* (2014) who showed that the MST is accompanied by a vertical transfer of holes from CuO_3 to CuO_2 planes. The other effect to be considered is that the re-emergent field will displace the ions of the layers in opposite directions towards their new equilibrium positions. Fig. 10 illustrates the temperature dependence of the c -axis bond length of Ba—O4, where a perfect correlation with the temperature dependence of the OP (Fig. 6) may be clearly

Figure 10

The temperature dependence of the bond length of Ba—O4 along the c axis in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ where a perfect correlation with the temperature dependence of OP (Fig. 6) may be clearly seen.

seen. The OP catastrophe (the ionic polarization catastrophe) can be considered as the origin of many structural instabilities and anomalies that have been observed by many research groups using different experimental methods in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ as well as other high-temperature superconductors near the critical temperature T_c (Schäfer *et al.*, 1988; Srinivasan *et al.*, 1988; Horn *et al.*, 1987; Cheng *et al.*, 1994; Molchanov & Simonov, 1998; Xu *et al.*, 1991; Wu *et al.*, 2001; Zhang *et al.*, 2008; Buttner *et al.*, 1992). The signature of this local field catastrophe in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ is the discontinuity in the Ba—O4 bond length along the c axis, observed at the superconducting transition temperature as illustrated in Fig. 10. The shift of the apical oxygen is limited to finite displacements because of the coupling at the unit-cell level of these local fields. In other words, the local ionic polarization field catastrophe at the critical temperature T_c triggers an out-of-plane correlation between the apical oxygen displacements at the unit-cell level and the onset of superconductivity. Fig. 11 illustrates the different charge transfers that take place inside the YBCO unit cell, at the critical temperature T^* of the pseudo-gap state or at the critical temperature T_c of the superconducting state, which is the consequence of the competition between inter-layer ionic interaction and the intralayer covalent bond nature of bonds inside the oxide.

Figure 11

Charge transfers inside the unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$; the intralayer covalency of CuO_2 induces an intersite transfer of charge (holes) from the in-plane oxygen O2,3 to the in-plane copper Cu2, increasing the interlayer ionicity (electron transfer from the copper of the plane towards the oxygen of the chain) which in turn causes the vanishing local field to re-emerge. This interplay leads to a pseudo-gap state at a critical temperature T^* or to a local field catastrophe that drives the compound to a superconducting state at a given critical temperature T_c .

Table 1

The OP with the corresponding physical states that result from the competition and interplay between the interlayer ionic interaction and the intralayer covalent nature of bonds in the cuprate oxide.

Order parameter ($C\text{ m}^{-2}$)	Compound state
$P < 0$	Insulator
$P = 0$	Insulator–metal transition
$P > 0$	Metal
$P = \infty (T_c)$	Metal–superconductor transition

One notes that the OP does not become infinite at the polarization catastrophe state because of the coupling at the unit-cell level of the local fields. At the MST, the asymmetry of the free charge carrier density will break locally the mirror reflection symmetry of the microscopic OP, leading to a pairing between the real current and the polarization current, or particle–anti-particle pairing characterized by CPT transformation, where C is the charge conjugation symmetry, P is the parity symmetry and T is the time reversal symmetry.

Table 1 summarizes the OP with the corresponding physical states that result from the competition and interplay between the interlayer ionic interaction and the intralayer covalent nature of bonds.

5. Conclusion

The main aim of this paper was to show that the most remarkable properties of the high-temperature superconducting cuprates, such as the insulator–metal transition and the metal–superconductor transition, originate from a competition and interplay between the ionic interlayer interaction and the intralayer covalent nature of bonds in these materials. A microscopic OP was proposed based on the local polarization field estimated from the ionic polarization at the sub-unit cell (one half of the unit cell) and it was demonstrated that it shows a strong temperature as well as chemical doping dependence, as a result of this competition.

The results show that the chemical doping changes the sign of the local ionic polarization field (the OP) compared with the parent insulator compound. Because of the strong intralayer covalent bond, an arrangement of the electronic structure is possible that consists of an interlayer transfer of electrons mainly from the covalent layer to the ionic adjacent layer. This charge transfer cancels the resulting local polarization field and drives hole doping of the p -like band of the in-plane oxygen which results in an IMT. However, the intralayer strong orbital hybridization between copper and oxygen induces an intersite transfer of charge (holes) that increases the interlayer ionicity and causes the vanishing local polarization field (the OP) to re-emerge. This competition and interplay leads to a local field catastrophe at a given critical temperature T_c that drives an MST. The asymmetry of the free charge carrier density breaks locally the mirror reflection

symmetry of the OP, leading to a pairing between the conduction current and the polarization current which is characterized by the CPT symmetry transformation.

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