La214 phase diagram features as a consequense of percolation over negative-U centers

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Abstract

The features of La214 phase diagram (including superconducting and stripe phases) are explained in terms of formation of negative-U center (NUS), ordering of localized doped carriers and percolation over NUS.

Key words: $La_{2-x}Sr_xCuO_4$; negative-U center; percolation; charge ordering

Recently we have shown [1] that the insulator-metal transition under doping passes through a particular dopant concentration range in which it becomes possible for local transitions of singlet electron pairs to occur from oxygen ions to two neighboring cations, while single electron transitions are still forbidden. This is a consequence of rigid localization of doped charges in charge-transfer insulator within a single unit cell that results in a local modification (on atomic scale) of electronic structure. For La214 the doped hole is localized in CuO_2 plane within oxygen octahedron and decreases the charge-transfer gap Δ_{ct} for 4 nearest Cu ions on $\sim$ 1.8 eV [1]. Thus the energy for electron transfer to these cations from neighboring ions decreases from Δ_{ct}^0 $\approx$ 2eV to $\Delta_{ct} \approx 0.2$ eV. If the doped charges are l=3a or $a\sqrt{5}$ apart, the pair of neighboring Cu ions arises for which Δ_{ct} is depressed (Fig. 1). (It is significant that for intermediate l=$a\sqrt{8}$ such Cu pairs are not formed).

As it was shown [1] such pair may operate as the negative-U center (NUC) due to making of bond state of two electrons and two holes like an intracrystal H_2 molecule. This possibility results from the fact that the distance between Cu ions in CuO_2 plane $a \approx 4$Å$\approx R_0\varepsilon_\infty$ eV, where R_0 - the distance between protons in H_2 molecule, ε_∞ - high-frequency dielectric constant, that is $\approx$4.5-5 for all HTS. Thus an additional decrease of $\delta\Delta_{ct}$ due to transition of two electrons to neighboring

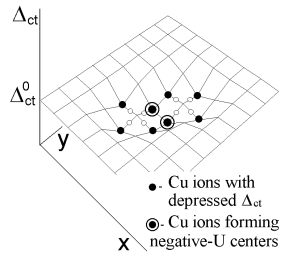

Fig. 1. In CuO_2 plane variation of charge-transfer gap Δ_{ct}. Two localized doped holes spaced $a\sqrt{5}$ occupy $p_{x,y}$ orbitals of oxygen ions denoted by open circles.

Cu ions $\delta\Delta_{ct} \approx \Delta E_H \approx 0.23$ eV. Thus Δ_{ct} vanishes for two-electron transitions to such pairs of Cu-ions while single electron transitions are still forbidden. The appearing hole pairs will occupy $\pi p_{x,y}$ oxygen orbitals [1] and will be localized in nearest NUC-vicinity. As NUS is formed only if doped carriers are spaced $3a$ or $a\sqrt{5}$, the joining of hole localization areas in percolation cluster is possible if infinite chain of NUS (or chain of doped carriers spaced $3a$ or $a\sqrt{5}$) is formed.

We insist that the distinctive feature of La214 system that permits the formation of percolation cluster from equidistant dopant ions is the special kind of dopant ordering over La sites. There are two reasons that determine the kind of dopant ordering: the long-distance field of deformations resulting from

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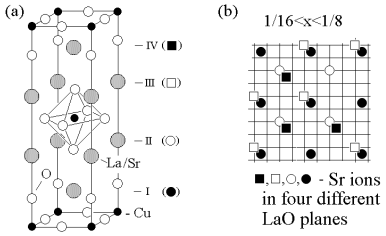

Fig. 2. a) $La_{2-x}Sr_xCuO_4$ unit cell; b) Sr ordering over La sites for $016<x<1/8$.

the difference of La and Sr(Ba) ion radii and repulsive interaction of doped carriers, that forbids them to be nearer than $2a$ [1]. At the same time X-ray study on La214 [2] reveals nonuniform substitution Sr for La in different LaO planes (Fig. 2a). As it was shown the substitution is carried out according to formula Cu-$La_{1-(x+y)/2}Sr_{(x+y)/2}$-$La_{1-(x+y)/2}Sr_{(x+y)/2}$-Cu-$La_{1-(x-y)/2}Sr_{(x-y)/2}$-$La_{1-(x-y)/2}Sr_{(x-y)/2}$-Cu $(0\leq y\leq x)$

We propose the next model of the partial-ordered substitution of Sr for La (Fig. 2). In I-th and II-d LaO planes Sr ions are completely ordered with equal concentration $x_i\leq x$ in square lattices with lattice parameter $L_i=1/\sqrt{x_i}$ ($L_i=\sqrt{8}$, $\sqrt{10}$, 4, $\sqrt{18}$, i.e. commensurable with CuO_2 lattice) so that the distance between the Sr ion in first plane and four nearest Sr ions in the second plane would be maximum. The rest x-x_i (per formula unit) is distributed uniformly over III-d and IV-th planes so that Sr ions in plane III(IV) occupy the sites over centers of squares formed by ordered Sr ions in plane II(I). Thus the holes doped to central CuO_2 plane by Sr-substitution for La in planes I and IV occupy the sites of square lattice with parameter $l_i=L_i/\sqrt{2}=1/\sqrt{2}$.

For a given x the domains with different x_i coexist if $x_i<x<2x_i$. So the ordering with $l_i=\sqrt{5}$ or 3 corresponding to the formation of NUC chains are possible for $1/10<x<1/5$ and $1/18<x<1/9$. The threshold of site percolation for a given kind of ordering is equal ~ 0.7. Therefore the percolation clusters of NUS will occur in the ranges $0.14<x<0.2$ and $0.077<x<0.11$. These intervals coincide with those of bulk high-temperature superconductivity on phase diagram of La214.

Further we are going to show that the proposed kind of ordering is able to account for other features of La214 phase diagram especially the periodic spin structure modulation (diagonal and parallel stripes) and the concentration dependence of commensurability $\delta=x$. In accordance with [3] we will consider that the doping result in the formation of AFM domains bordered by localized doped holes and that the directions of magnetization in neighboring domains are twisted. Firstly we guess the spin structure pattern for some completely

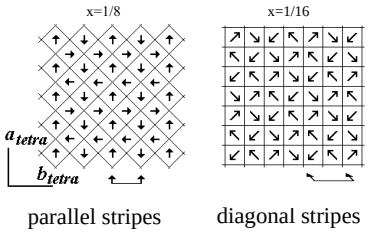

Fig. 3. AFM domain texture for completely ordered doped hole distributions (x_0=1/8 and 1/16) .

ordered doped hole distributions (x_0=1/8 and 1/16) showing the periodic spin structure modulation that observed in experiments.

Fig. 3a shows the completely ordered hole distribution for (x_0=1/8 when these holes form square lattice with $l=\sqrt{8}$ or 4. Only the occupied sites that border the AFM domains are shown. The arrows point to magnetization directions in individual domains. This spin structure corresponds to the "parallel stripes" picture. It is seen that the period of spin modulation T equals to doubled domain dimension in the modulation vector direction, i.e. $T=2\sqrt{2}l=8$, and $\delta=1/8=x$. The completely ordered hole distribution for $x=1/16$ (Fig. 3b) can be obtained by the rotation of Fig. 3a by 45^0. This hole distribution corresponds to the "diagonal stripes" picture. In tetragonal axis $T=16$ and $\delta=1/16=x$.

Now we consider the partial site occupation at $x_0/2<x<x_0$ (x_0=1/8 and 1/16) on the square lattices with $l=\sqrt{8}$ and 4. In this case the CuO_2 plane breaks into AFM domains bordered by occupied sites (or by doped carriers). It can be easily shown that in the case under consideration the mean magnetic period (that can be inferred from neutron diffraction experiments) T is proportional to $1/x$. At $1/32<x\leq 1/16$ we will have "diagonal stripes" with $\delta=x$ in tetragonal axis, and at $1/16<x\leq 1/8$ the "parallel stripes" are formed with $\delta=x$, too. At $1/32<x\leq 1/16$ we will have the static spin structure. But at $1/16<x\leq 1/8$ the "static stripes" can be observed only in the ranges $1/16<x<0.077$ and $0.11<x<0.14$ since the appearance of percolative conductivity at $0.077<x<0.11$ results in destruction of static magnetic correlations, that can be observed for this range as dynamic correlations in inelastic neutron diffraction. Thus the proposed mechanism of NUS formation together with the model of doped carrier ordering allow to account for all features of the La214 phase diagram.

References

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