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METAL-INSULATOR TRANSITIONS IN DOPED *La*-BASED SUPER CONDUCTORS WITH SMALL-RADIUS DOPANTS

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In this work, we study the possibility of realizing two distinct mechanisms of metal-insulator transitions in hole-doped cuprates induced by the localization of charge carriers near the small-radius impurities and in a deformable lattice (i.e. in the absence of impurities). The purpose of this research is to determine the criteria (i.e. conditions) for the existence of the localized states of hole carriers and solve the problem of metal-insulator transitions in La-based cuprates. The advantage of La-based cuprate versus other types of cuprates is that two distinct metal-insulator transitions in La-based cuprates driven by the strong carrier-impurity-phonon and carrier-phonon interactions occur simultaneously in a wider doping range from the lightly doped to heavily doping regime. We show that at very low doping, the separate levels of hole carriers localized near impurities and in a deformable lattice are formed in the charge-transfer gap of the cuprates. As the doping level increases towards underdoped region, the energy levels of such charge carriers start to form energy bands which gradually broaden with increasing doping. We propose a new two-carrier cuprate superconductor model for studying two distinct metal-insulator transitions occurring simultaneously in hole-doped La-based cuprate compounds. We demonstrate that when hole carriers reside in impurity and polaron bands, these metal-insulator transitions in La-based superconductors with small-radius dopants occur accordingly in a wide doping range and relatively lower doping levels.

Keywords: Hole-doped cuprates; Carrier localization; Metal-insulator transitions.

Introduction

The mechanisms of the localization of charge carriers and metal-insulator transitions in undoped and doped materials have been central problems of the condensed matter physics for many decades [1-10]. According to the one-electron band theory, crystalline solids are metals with a partially filled valence band or insulators with a completely filled valence band. Such a classification of solids into metals and insulators was originally proposed by Wilson [11]. According to the Wilson's band theory of non-interacting electrons, metal-insulator transitions in crystalline solids can occur when two band will overlap due to the change in volume (under pressure) or temperature of the materials. This one-electron band theory has been very successful in describing many crystalline materials. But it is turned to be inadequate for transition metal oxides with a partially filled *d*-electron band, which are insulators [6,7].

Since in conventional simplified band theory, the most important features of many-body systems, such as strong Coulomb repulsion between electrons (i.e., electron-electron correlation), disorder in atomic and electronic subsystems and electron-lattice interaction were ignored. Further, Mott [1] and Anderson [12] suggested the ideas of the localization of electrons and metal-insulator transitions due to the strong electron-electron correlation and structural disorder, respectively. These correlation- and disorder-induced metal-insulator transitions called Mott and Anderson metal-insulator transitions were discussed as the basic mechanisms of the localization of charge carriers in crystalline and non-crystalline solids [3,6,7,9]. Mott considered a half-filled *d*-electron band (with bandwidth W and on-site Coulomb repulsion U_d between electrons) or a perfect crystal lattice of one-electron hydrogen-like atoms with the lattice constant a. According to Mott, the electrons of the half-filled valence band are delocalized at small a (or large W) satisfying the condition $W/U_d > 1$ and characterized by metal-like conductivity. When a is increased, the band is continuously narrowed. The electrons of this narrow band are localized at their respective atoms and the crystalline material is converted into an antiferromagnetic insulator due to the splitting of the half-filled band into upper and lower Hubbard bands at $W/U_d < 1$. This model of a perfect crystal structure is not relevant to real crystalline solids in which there is a certain degree of disorder (e.g., vacancies, impurities, displaced atoms, and deformed chemical bonds). Therefore, Anderson considered the possibility of the localization of

non-interacting electrons due to disorder. Anderson used a crystalline array of potential wells with a random potential V_0, varying between the limits $\pm(1/2)V_0$.

Metal-insulator transitions in doped semiconductors and copper-oxide (cuprate) compounds have been previously studied for the case of the existence of one type of charge carriers [3,6,7,9,13]. However, in these materials, doped charge carriers can reside near dopants (impurities) as bound carriers and in defect-free regions of the crystal lattice as polaronic carriers. Therefore, such two types of charge carriers can coexist in doped semiconductors and high-temperature cuprate superconductors, and the criterion for metal-insulator transition in the case of two coexisting charge carriers will differ from the criterion formetal-insulator transition obtained in the one-carrier semiconductor or high-T_c superconductor model [14]. These circumstances were not previously considered in the studying metal-insulator transitions in doped materials. In this work, we will consider the possibility of realizing two different mechanisms of metal-insulator transitions occurring simultaneously in hole-doped *La*-based cuprate superconductors with small radius dopants, where two types of charge carriers are residing in the impurity and polaron bands. The goal of choosing *La*-based cuprates for study the mechanisms of metal-insulator transitions is that these systems (as distinct from other types of cuprate compounds) allow us to study two different types of metal-insulator transitions occurring simultaneously in a wide doping range from the lightly doped to heavily doped regime and to compare the key differences between these metal-insulator transitions, which are driven by the strong carrier-impurity-phonon and carrier-phonon interactions, in hole-doped *La*-based cuprates.

1. New criteria for metal-insulator transitions indoped *La*-based cuprates defined within two-carrier cuprate super conductor model

If the electron-phonon interactions near dopants (impurities) are weak, the simple hydrogen-like impurity centers are formed in doped cuprates [9]. Such a situation is realized in $La_{2-x}Sr_xCuO_4$ (LSCO) and $La_{2-x}Ba_xCuO_4$ (LBCO), in which the radius of both the Sr^{2+} and the Ba^{2+} is larger than that of La^{3+}, so that for Sr^{2+} and Ba^{2+} the sign of the deformation potential is negative [15]. If follows that the hole-lattice interactions near the large-radius dopants in LSCO and LBCO are suppressed by the repulsive impurity potential and hole carriers are localized at a distance from the dopants Sr^{2+} and Ba^{2+} and form the hydrogen-like impurity centers. In this case the Mott's metal-insulator transition in the single-carrier solid model is driven by the electron correlation in such impurity centers and can occur only very low doping levels ($x\leq0.02$) in LSCO and LBCO and the other type of metal-insulator transition in these materials driven by the strong hole-lattice interactions can take place also in the single-carrier solid model at more higher doping levels.

Another interesting question is how small-radius dopants (impurities) in doped cuprates affect the carrier localization and related metal-insulator transition. The signs of deformation potentials of holes and small-radius dopants are positive in $La_{2-x}Ba_{x-y}M_yCuO_4$ (where $M=Ca^{2+}$) and $La_{2-x-y}Nd_ySr_xCuO_4$, where the carrier-impurity-phonon interaction is attractive near the small-radius dopants (e.g. Ca^{2+} and Nd^{3+} ions). Therefore, the substitution of small-radius ions Ca^{2+} and Nd^{3+} for La^{3+} ions in *La*-based cuprates leads to the combined impurity- and phonon-assested self-trapping of hole carriers with the formation non-hydrogen-like localized impurity states which can form impurity band at high doping levels. We assume that some part of hole carriers are localized near small-radius dopants and other part of hole carriers are self-trapped in a deformable lattice with the formation of large polarons. We now take into account these circumstances in the study of the metal-insulator transitions driven by the strong carrier-impurity-phonon and carrier-phonon interactions in *La*-based cuprates with small-radius dopants ($Ca^{2+}$and Nd^{3+}). We argue that when the hole carriers are localized near impurities and in a deformable lattice with the formation of impurity centers and polarons, as observed in *La*-based cuprates [16], the conditions for carrier localization or criteria for metal-insulator transitions are quite different. In the following, we will determine these new criteria for metal-insulator transitions in a two-carrier cuprate super conductor model that is better applicable to doped *La*-based cuprates with small-radius dopants than other La-based cuprates with large-radius dopants.

It is natural to assume that the impurity centers and polarons can form superlattices and impurity and polaron bands in doped cuprates. When two coexisting types of charge carriers in doped materials are residing in the impurity and polaron bands, the Fermi energy ε_{FI} of charge carriers in the impurity band and the Fermi energy ε_{Fp} in the polaron band can be defined as

$$\varepsilon_{FI} = \hbar^2(3\pi^2 f_I n)^{2/3}/2m_I \tag{1}$$

and

$$\varepsilon_{Fp} = \hbar^2(3\pi^2(1-f_I)n)^{2/3}/2m_p \tag{2}$$

where f_I is the fraction of charge carriers residing in the impurity band, m_I is the mass of such charge carriers, m_p is the mass of large polarons, n is the concentration of doped charge carriers.

In a two-carrier cuprate superconductor model, the conditions for carrier localization or the new criteria for metal-insulator transitions will be different from the criteria for metal-insulator transitions defined in the single-carrier cuprate superconductor model [14] and can be written as

$$\frac{E_I}{\varepsilon_{FI}} = \frac{2E_I m_I}{\hbar^2(3\pi^2 f_I n)^{2/3}} \geq 0.5\frac{a_I}{R_I}, \tag{3}$$

and

$$\frac{E_p}{\varepsilon_{Fp}} = \frac{2E_p m_p}{\hbar^2(3\pi^2(1-f_I)n)^{2/3}} \geq 0.5\frac{a_p}{R_p}, \tag{4}$$

where E_I is the binding energy of the charge carriers which are bound to the impurity centers, a_I is the lattice parameter of the impurity superlattice, R_I is the radius of the impurity center, E_p is the polaron binding energy, a_p is the lattice parameter of the polaron superlattice, R_p is the polaron radius. Now, the criteria (3) and (4) for certain level of doping $n=n_c$ can written as

$$x = x_{cI} = \frac{n_c}{n_a} = \frac{1}{3\pi^2 f_I n_a}\left[\frac{4m_I E_I R_I}{\hbar^2 a_I}\right]^{3/2} \tag{5}$$

and

$$x = x_{cp} = \frac{n_c}{n_a} = \frac{1}{3\pi^2(1-f_I) n_a}\left[\frac{4m_p E_p R_p}{\hbar^2 a_p}\right]^{3/2} \tag{6}$$

where $n_a = 1/V_a$ is the density of the host lattice atoms, V_a is the volume per CuO_2formula unit in the cuprates.

We assume that the impurities centers and polarons form simple cubic superlattices. For simple cubic superlattices of impurity centers and polarons, lattice parameters can be determined as $a_I = 2R_I$ and $a_p = 2R_p$.Therefore, applying the criterions (5) and (6) for metal-insulator transitions to these impurity centers and polarons, we obtain the following critical doping levels corresponding to the metal-insulator transitions driven by the strong carrier-impurity-phonon and carrier-phonon interactions:

$$x_{cI} = \frac{V_a}{3\pi^2 f_I \hbar^3}[2m_I E_I]^{3/2} \tag{7}$$

and

$$x_{cp} = \frac{V_a}{3\pi^2(1-f_I)\hbar^3}\left[2m_p E_p\right]^{3/2}. \tag{8}$$

At such critical doping levels, the transitions from insulating state to metallic state or from metallic state to insulating state occur in doped cuprates. The quantity of both E_I and E_p depends on the high-frequency ε_∞ and static ε_0 dielectric constants, as well as on the ratio $\eta=\varepsilon_\infty/\varepsilon_0$.

2. Results and discussion

The expressions (7) and (8) for x_{cI} and x_{cp} contain two pairs of key parameters (m_I, E_I and m_p, E_p) characterizing the effective masses of charge carriers in their localized states and carrier-impurity-phonon and carrier-phonon interactions, which result in the formation of the localized impurity state and polaronic state. Using the criteria (7) and (8), one can determine the possibility of realizing different mechanisms of metal-insulator transitions in doped *La*-based cuprate compounds with small-radius dopants. In particular, these expressions allow us to calculate the critical doping levels x_{cI} and x_{cp}, at which the metal-insulator transitions occur in $La_{2-x}Ba_{x-y}Ca_yCuO_4$ and $La_{2-x-y}Nd_ySr_xCuO_4$. The volume per CuO_2 formula unit V_a in *La*-based cuprate superconductors is equal to 190 *Å*.

2.1. Metal-insulator transitions driven by the strong carrier-impurity-lattice interactions in doped cuprate superconductors $La_{2-x}Ba_{x-y}Ca_yCuO_4$ and $La_{2-x-y}Nd_ySr_xCuO_4$ with small-radius dopants

Using the expression (7), we calculate the critical doping levels x_{cI}, at which the metal-insulator transitions driven by the strong carrier-impurity-lattice interactions occur in $La_{2-x}Ba_{x-y}Ca_yCuO_4$ and $La_{2-x-y}Nd_ySr_xCuO_4$. By taking $m_I = 2.0m_e$, E_I=(0.0741-0.1240) eV (at ε_∞=3.5-4.5 and η= 0.02) [17] and f_I= 0.5, we find the following critical doping levels x_{cI}=0.098-0.213 at which the metal-insulator transitions occur in $La_{2-x}Ba_{x-y}Ca_yCuO_4$ and $La_{2-x-y}Nd_ySr_xCuO_4$ from the underdoped to heavily overdoped regime in the regions of the crystal lattice containing impurities. The calculated results for x_{cI} at η= 0.02 and different values of E_I and ε_∞ are presented in Table 1. From these results, it follows that when ε_∞ decreases, the metal-insulator transitions occur at more higher doping levels.

Table 1. The calculated critical doping levels x_{cI} at η= 0.02 and different values of E_I and ε_∞

E_I=0.1240 eV, ε_∞=3.5		E_I=0.0943 eV, ε_∞=4		E_I=0.0741 eV, ε_∞=4.5	
f_I	x_{cI}	f_I	x_{cI}	f_I	x_{cI}
0.5	0.213	0.5	0.141	0.5	0.098

2.2. Metal-insulator transitions driven by the strong carrier-lattice interactions in the cuprate superconductors $La_{2-x}Ba_{x-y}Ca_yCuO_4$ and $La_{2-x-y}Nd_ySr_xCuO_4$ with small-radius dopants

Using the expression (8), we calculate the critical doping levels x_{cp}, at which the metal-insulator transition driven by the strong carrier-lattice interactions occur in $La_{2-x}Ba_{x-y}Ca_yCuO_4$ and $La_{2-x-y}Nd_ySr_xCuO_4$. In our calculations, we now take $m_p = 1.8m_e$ and use the values of E_p=(0.0640 -0.1063) eV (at ε_∞=3.5-4.5 and η= 0.02) [17]. When the fraction of charge carriers in the polaronic band is equal to f_p=1-f_I= 0.5, we find the following critical doping levels x_{cp}=0.067-0.144 at which the metal-insulator transitions occur in $La_{2-x}Ba_{x-y}Ca_yCuO_4$ and $La_{2-x-y}Nd_ySr_xCuO_4$ from the underdoped to optimally doped regime in the regions of the crystal lattice without impurities. The calculated results for x_{cp} at η= 0.02 and different values of E_p and ε_∞ are presented in Table 2. As can be seen from Table 2, the metal-insulator transitions occur at more higher doping levels with decreasing ε_∞ from 4.5 to 3.5.

Table 2. The calculated critical doping levels x_{cp} at η= 0.02 and different values of E_p and ε_∞

E_p=0.1063 eV, ε_∞=3.5		E_p=0.0811 eV, ε_∞=4		E_p=0.0640 eV, ε_∞=4.5	
f_p	x_{cp}	f_p	x_{cp}	f_p	x_{cp}
0.5	0.144	0.5	0.096	0.5	0.067

Conclusion

We have studied the possibility of realizing two new and fundamentally different mechanisms of metal-insulator transitions in *La*-based cuprate compounds with small-radius dopants (impurities) in a pertinent two-carrier superconductor model. We have demonstrated that the proposed two-carrier *La*-based cuprate superconductor model is more realistic than the previously studied single-carrier model of this superconductor, which was considered by many researchers (see Refs. [3,6,9,11,12,14]). This new model predicts much more reliable results for metal-insulator transitions in doped *La*-based cuprates than other existing results predicted by the single-carrier cuprate superconductor model. We have argued that none of the previously proposed theoretical models considering only one type of localized charge carriers in doped cuprates, are capable of accounting for the full body of experimental data [6,9,18-21] and the metal-insulator transitions observed in a wide doping range from the lightly doped to heavily doped regime in a *La*-based cuprates with small-radius dopants. The scientific significance of our obtained results is that the metal-insulator transitions in *La*-based cuprate compounds occur not only in underdoped regime in accordance with experimental results [18] but also in the two distinct doping ranges, namely, from the underdoped to

optimally doped ($0.06 \leq x \leq 0.15$) and from the underdoped to heavily overdoped ($0.06 \leq x \leq 0.21$) regimes in full accordance with the existing experimental results [18-21].We have shown that the metal-insulator transitions in these cuprate superconductors are induced by the localization of hole carriers near the small-radius dopants and in the regions without such impurities. We have found that the criteria for metal-insulator transitions driven by the hole-impurity-lattice and hole-lattice interactions are quite different. According to our two-carrier cuprate superconductor model, the metal-insulator transitions occur first in the regions without small-radius impurities at intermediate doping levels ($x<0.15$) and then in the regions with such impurities at more higher doping levels reaching up to $x \geq 0.21$. Thus, our results indicate that in *La*-based cuprate superconductors, two distinct metal-insulator transitions occur simultaneously in a wide range of doping, namely, from the lightly doped to heavily overdoped regime, as observed in various experiments [18-21]. We note that in some experiments (see Ref. [18]) the dopant concentrations in $Bi_2Sr_{2-x}La_xCuO_{6+d}$ and $La_{2-x}Sr_xCuO_4$ for study of metal-insulator transitions were chosen the underdoped and optimally doped regimes respectively, and in other experiments, the concentration of dopants in $La_{2-x-y}Nd_ySr_xCuO_4$ and $La_{2-x}Sr_xCuO_4$ was selected from lightly doped mode ($x=1/8$) to heavily doped mode ($x > 0.2$) [20,21].

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REFERENCES

1. Mott N. F. The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals. *Proc. Phys. Soc. London*. 1949, Vol. A62, pp. 416 - 422.

2. Hubbard J. Electron correlations in narrow energy bands. II. The degenerate band case. *Proc. Roy. Soc. London.* 1964, Vol. A277, pp. 237-259; Electron correlations in narrow energy bands. III. An improved solution. *Proc. Roy. Soc. London*. 1964, Vol. A281, pp. 401-419.

3. Mott N.F. *Metal-Insulator Transitions*. Taylor and Francis, London, 1990, 286 p.

4. Lavrov A.N., Gantmakher V.F. Low-temperature resistivity of under doped cuprates. *Phys. Usp.* 1998, Vol.41, pp. 223-226.

5. Abrikosov A.A. Resonant tunneling in high-T_c superconductors. *Phys.Usp.* 1998, Vol.41, pp. 605-616.

6. Imada M., Fujimory A., Tokura Y. Metal-insulator transitions. *Rev. Mod. Phys.* 1998, Vol. 70, pp. 1039-1263.

7. Walz F. The Vervey transition- a topical review. *J. Phys.: Condens. Matter.*2002, Vol.14, pp. R285-R340.

8. Vedeneev S.I. High temperature superconductors in strong and superstrong magnetic fields. *Usp. Fiz. Nauk*, 2012, Vol.182, pp.669-676.

9. Dzhumanov S. *Theory of Conventional and Unconventional Superconductivity in the High-T_c Cuprates and Other Systems*. Nova Science Publishers, New York, 2013, 356 p.

10. Dzhumanov S., et al. Formation of intermediate coupling optical polarons and bipolarons. *Phys. Lett. A.* 2019, Vol. 383, pp.1330-1335.

11. Wilson A. H. The theory of Electronic Semi-Conductors. *Proc. Roy. Soc. London*. 1931, Vol. A133, pp. 458-491; The theory of electronic semi-conductors. II. *Proc. Roy. Soc. London*, 1931, Vol. A134, pp. 277-287.

12. Anderson P.W. Absence of Diffusion in Certain Random Lattices. *Phys. Rev.*1958, Vol. 109, pp. 1492-1505.

13. Damascelli A., Hussain Z., Shen Z.X. Angle-resolved photoemission studies of the cuprate superconductors. *Rev. Mod. Phys.* 2003, Vol.75, pp.473-541.

14. Dzhumanov S., Kurbanov U.T. The new metal-insulator transitions and nanoscale phase separation in doped cuprates. *Super lattices and Microstructures*, 2015, Vol.84, pp. 66-71.

15. Toyozawa Y. Electron induced lattice relaxations and defect reactions. *Physica B*, 1983, Vol.116, pp. 7-17.

16. Kastner M.A., Birgeneau R.J., Shirane G., Endoh Y. Magnetic, transport and optical properties of monolayer copper oxides. *Rev. Mod. Phys.*1998, Vol. 70, pp. 897-928.

17. Dzhumanov S., et al. Possible mechanisms of carrier localization, metal-insulator transitions and stripe formation in homogeneous hole-doped cuprates. *J. Phys. Chem. Solids.* 2012, Vol.73, pp. 484- 494.

18. Ono S., et al. Low-temperature normal state of $Bi_2Sr_{2-x}La_xCuO_{6+d}$: comparison with $La_{2-x}Sr_xCuO_4$. *Physica C.* 2001, Vol.357-360, pp. 138-141.

19. Anshukova N.V., et al. The effect of super structural ordering on the properties of high-temperature oxide superconductor systems. *Zh. Eksp. Teor. Fiz.* 2003, Vol. 123, pp. 1188-1199. [in Russian]

20. Sakita Sh., et al. Structural transitions and localization in $La_{2-x-y}Nd_ySr_xCuO_4$ with *p* similar to 1/8. *J. Phys. Soc. Jpn.* 1999, Vol.68, pp. 2755-2761.

21. Koike Y., et al. *Cu*-site-substitution effects on the 1/8 anomaly in the high-T_c cuprates and on the anomaly at $x=0.21$ in $La_{2-x}Sr_xCuO_4$. *Physica C.* 2001, Vol. 357-360, pp. 82-88.

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