Possible states of charge carriers in thin multilayered superconductive ceramics

ABSTRACT

This paper analyzes behavior (spectra and states) of the elementary charge carriers in anisotropic perovskite structures, such as modern superconducting ceramics. Translational symmetry of the atom (ion) distribution of the electron (or hole) system is broken by atomic/ionic/molecular sputtering and doping, as well as due to existence of two boundary surfaces. This is a charge carrier’s model of high-temperature superconductors in which the observed symmetry breaking orthogonal to CuO planes was treated as a perturbation. The single-particle fermion’s wave functions and the possible energies of charge carriers were determined.

Keywords: Charge carriers, boundaries, anisotropy, energy states and spectra, one-particle wave functions.

1. INTRODUCTION

The answer to the question of the oxide ceramics superconductivity mechanism must be undoubtedly sought in the phonon subsystem, in the elementary charges subsystem as well as in the interaction of these subsystems. With regard to the very anisotropic structure of the superconductive ceramics [1–4], we have attempted to construct a theoretical model conveying the broken translational symmetry of atoms (or molecules) arrangement along one direction in the crystal lattice, the difference of masses of these molecules and the presence of two boundary planes along this direction [5–9].

The phonon system is drawn out in this model [2,4–9]. We have determined the phonon states and their energy spectra and we have shown that, due to the broken crystal symmetry (actually because of deformed and tiny granular structure), the phonons of optical type owning the energy gaps are present here. The next task that we have attempted to solve is to determine and analyze the spectra of charge carriers (electrons or holes), Landau criterion, the probabilities of states and entropy within the same model [10–12].

2. FORMATION OF THE MODEL STRUCTURE

In order to obtain Hamiltonian of the charge carriers in the structure with broken translational symmetry, it is the most suitable to start with the standard Hamiltonian of electron system in an ideal infinite structure:

\[ H_{id} = \sum_{k} \frac{\hbar^2 k^2}{2m'} a_k^+ a_k, \]

where \( m' \) is charge carriers effective mass, while \( a_k^+ \) and \( a_k \) are Fermi’s creation and annihilation operators of charge carriers with momentum \( \frac{\hbar k}{2m} \) and energy \( \frac{\hbar^2 k^2}{2m} \) [13–15]. If we go over to the configuration space using the transformations:

\[ a_k = \frac{1}{\sqrt{N}} \sum_{n} a_{n} e^{i kn}; \quad a_k^+ = \frac{1}{\sqrt{N}} \sum_{n} a_{n}^* e^{i kn}, \]

where \( N \) is the number of molecules in the considered structure, we get:

\[ H_{id} = \sum_{n} V a_n^* a_n - \sum_{\hat{n},\hat{m}} W_{\hat{n}\hat{m}} a_{\hat{n}}^* a_{\hat{m}}^+ , \]

where \( V = \frac{1}{N} \sum_{k} \frac{\hbar^2 k^2}{2m'} \) and \( W_{\hat{n}\hat{m}} = \frac{1}{N} \sum_{k} \frac{\hbar^2 k^2}{2m'} e^{i(k-\hat{m}) \hat{n}} \).

Due to the canonicity of the transformation (2), the operators \( a_k^+ \) and \( a_k \) are also Fermi’s operators.
Let us recall the most important assumptions of our model: we consider the tetragonal, i.e. generalized cubic structure with very high anisotropy along the z axis. It means that the lattice constant in this direction \(a_z\) is a few times larger than the lattice constant \(a_x, a_y\) in the directions \(x\) and \(y\). The translational symmetry is fully conserved in the \(XY\) planes, while the symmetry of the masses arrangement along the \(z\) direction is broken (during the doping of the ceramic structure by the introducing of foreign atoms, the sputtered atoms locate along this direction because it is energetically most convenient). We also assume here that the structure under consideration is a thin film. It means that the components of lattice vector \(\mathbf{n} = (n_x, n_y, n_z)\) vary in the following way:

\[
n_r = \left(\frac{N_r}{2}, \frac{N_r}{2}, 0\right); \quad \mathbf{r} = (x, y); \quad n_z \in [0, N_z]
\]

The numbers of atoms \(N_r\) and \(N_z\) along the directions \(x\) and \(y\), respectively, may be indefinitely high, since we have the translational symmetry along these directions. The number of atoms along \(z\) direction \(N_z\) is limited. The above described model, i.e. the highly anisotropic matrix along the \(z\) direction, necessarily doped with foreign atoms, can be used for getting some qualitative conclusions about the superconductive ceramics behavior. It is known [1−4] that the ceramic oxides are anisotropic along one privileged direction and that the superconductive state is realized by doping. But the real structure of the ceramic oxides – perovskites is approximated by the tetragonal structure. It is also assumed in the model that the sputtering is symmetric on the both of boundary planes: \(n_z = 0\) and \(n_z = N_z\) and between the layers \(n_z = 0\) and \(n_z = 1\) (as well as between the layers \(n_z = N_z - 1\) and \(n_z = N_z\)) foreign particles are placed, in such a way that the structure of the doped matrix is unchanged near the middle of the film.

If the behavior of the quantities from \((3)\) may be expressed by the law:

\[
W_{\text{slh}} = \frac{W_0}{|\mathbf{n} - \mathbf{m}|^h}; \quad W_0 > 0; \quad h > 0,
\]

in the nearest-neighbors approximation we get:

\[
W_{n_z,n_z+1} = \frac{W_0}{a_{s_z}^0}; \quad s = (x, y, z).
\]

According to the described view of the doping, it is obvious that lattice constant \(a_z\) in the doped structure becomes dependent on the position \(n_z\), i.e. \(a_z \rightarrow a_z (n_z)\). Because of the symmetry on the boundary planes, i.e. boundary layers: \(a_z(0) = a_z(N_z) = \frac{a_z}{n_0 + 1}\); \(a_z(N_z/2) = a\), we may take:

\[
a_z(n_z) = a_z \left(1 - \frac{n_0}{n_0 + 1} \beta_z^2\right); \quad \beta_z^2 = \frac{2n_z}{N_z} - 1.
\]

The dependence of the lattice constant on the index \(n_z\) causes the dependence of the interaction along \(z\) direction on the index \(n_z\), i.e.

\[
W_z \rightarrow W_z(n_z) = \frac{W_0}{a_z^0(n_z)} = \frac{W_0}{a_z^0(n_0)} \left(1 - \beta_z^2 \frac{n_0}{n_0 + 1}\right)^{-h} = W_z(1 + \Phi \beta_z^2)
\]

where \(\Phi = \frac{n_0}{n_0 + 1}\). The interactions \(W_x\) and \(W_y\), according to the described picture, are unchanged. We must notice that the last two expressions are valid for even \(N_z\). But, for large enough \(N_z\) \((N_z = N_z - 1)\), or during the transition from \(n_z\) to continual variable \(z\), the deviations from the formulas \((6)\) and \((7)\) for odd \(N_z\) are not essential. The values of \(V\) are not dependent on the index of the site; because of they are unchanged during the doping. Hence we can write the Hamiltonian of the doped structure in the form:

\[
H = H_B + H_V,
\]

where:

\[
H_B = \sum_{\mathbf{n}_r} \left[ a^n_{\mathbf{n}_r,0} V a_{\mathbf{n}_r,0} - W_x \left(a_{\mathbf{n}_r,0} + a_{\mathbf{n}_r,0}^\dagger\right) - W_y \left(a_{\mathbf{n}_r,0} + a_{\mathbf{n}_r,0}^\dagger\right) - W_z(1 - \Phi) a_{\mathbf{n}_r,0}^\dagger\right] + \quad (9)
\]

\[
+ a^n_{\mathbf{n}_r,N_z} \left[ V a_{\mathbf{n}_r,N_z} - W_x \left(a_{\mathbf{n}_r,N_z} + a_{\mathbf{n}_r,N_z}^\dagger\right) - W_y \left(a_{\mathbf{n}_r,N_z} + a_{\mathbf{n}_r,N_z}^\dagger\right) - W_z(1 - \Phi) a_{\mathbf{n}_r,N_z}^\dagger\right]
\]

and, as we can see, it is related to the boundary layers \((n_z = 0\) and \(n_z = N_z\)), where obviously \(W_{n_z,N_z,0,n_z,N_z-1} = W_{n_z,N_z,n_z,n_z+1} = 0\), and for \(H_v\) we find:

\[
H_V = \sum_{\mathbf{n}_r} \left[ a^n_{\mathbf{n}_r,0} V a_{\mathbf{n}_r,0} - W_x \left(a_{\mathbf{n}_r,0} + a_{\mathbf{n}_r,0}^\dagger\right) - W_y \left(a_{\mathbf{n}_r,0} + a_{\mathbf{n}_r,0}^\dagger\right) - W_z(1 - \Phi) a_{\mathbf{n}_r,0}^\dagger\right] + \quad (10)
\]

\[
+ a^n_{\mathbf{n}_r,N_z} \left[ V a_{\mathbf{n}_r,N_z} - W_x \left(a_{\mathbf{n}_r,N_z} + a_{\mathbf{n}_r,N_z}^\dagger\right) - W_y \left(a_{\mathbf{n}_r,N_z} + a_{\mathbf{n}_r,N_z}^\dagger\right) - W_z(1 - \Phi) a_{\mathbf{n}_r,N_z}^\dagger\right].
\]
3. SINGLE-PARTICLE STATES

We shall analyze the system described by Hamiltonian (8) using the orthonormalized single-electron state functions:

$$|\psi\rangle = \sum_{n_x,n_y,n_z} A_{n_x,n_y,n_z} a_{n_x,n_y,n_z}^\dagger |0\rangle;$$

$$\sum_{n_x,n_y,n_z} |A_{n_x,n_y,n_z}|^2 = 1. \quad (11)$$

We obtain the equations for finding the coefficient $A_{n_x,n_y,n_z}$ using the equations of motion for operators $a_{n_x,n_y,n_z}$. From the equation:

$$a_{n_x,n_y,n_z}(t) = a_{n_x,n_y,n_z}(0)e^{i\omega t}, \quad \text{where} \quad \omega = E / \hbar, \quad \text{it follows:}$$

$$E a_{n_x,n_y,n_z} - \left[ a_{n_x,n_y,n_z}, H \right] = C_{n_x,n_y,n_z}; \quad C_{n_x,n_y,n_z} = 0. \quad (12)$$

On the basis of equations (8 - 10) and (12), we form operators: $C_{n_x,n_y,n_z}$, $C_{n_x,n_y,n_z}$, and $C_{n_x,n_y,n_z}$. After applying them to the functions (11) and using the general substitution:

$$\alpha_{n_x,n_y,n_z} = \alpha_{n_x} e^{i(n_x k_x + n_y k_y)},$$

where $k_j = \frac{2\pi}{N_j} \nu_j; \quad j = (x,y); \quad \nu_j \in \left\{ -\frac{N_j}{2} + \frac{N_j}{2} \right\}$

and on the basis of the fact that $V = 2 \sum W_j$, we find the following system of $N_x + 1$ difference equations for $n_x = 0, n_x = N_x$ and for $1 \leq n_x \leq N_x - 1$, respectively:

$$(E - 4Q - 2W_x) |A_0\rangle + W_x (1 - \Phi) |A_{n_x=1}\rangle = 0,$$

$$(E - 4Q - 2W_x) |A_{n_x} \rangle + W_x (1 + \Phi) |A_{n_x-1}\rangle = 0. \quad (13)$$

$$(E - 4Q - 2W_x) = Q |a_{x,k_x}^2 + a_{y,k_y}^2 - \frac{a_{x,k_x} a_{y,k_y}}{2} \rangle = 0,$$

where $Q = Q_{n_x,k_x} = W_x \sin^2 \frac{a_{x,k_x}}{2} + W_y \sin^2 \frac{a_{y,k_y}}{2}$

We shall perform the further analysis in the continual approximation in order to avoid the complications arising during the determination of the coefficient $a_{n_x}$ from the system of difference equations (13). Introduction the continual variable $z$ through: $n_x \to z/\bar{a}_z$. $(N_x \to L/\bar{a}_z)$ causes the following transformations of the expressions (7) and (6):

$$a_{n_x,n_y,n_z} \to a_{z}(z) = a_{n_x} \left[ 1 - \frac{n_x}{n_0 + 1} \left( \frac{2z}{L} \right)^2 \right],$$

$$W_{n_x,n_y,n_z} \to W_z(z) = W_x \left[ 1 + \phi \left( \frac{2z}{L} \right)^2 \right]. \quad (14)$$

The coefficients $A_{n_x}$ will be transformed in the following way:

$$A_{n_x} \to A(z); \quad A_{n_x+1} + A_{n_x-1} \to A(z - a_z) + A(z - a_z);$$

$$A(z \pm a_z) = A(z) \pm \frac{a_z}{2} \frac{d^2 A}{dz^2} + \frac{a_z^2}{2} \frac{d^2 A}{dz^2} ;$$

$$\tilde{a}_z = a_z(z) = \frac{1}{L} \left[ \int dz z a_{z}(z) = a_z (2\mu + 3) / \left( 3(n_0 + 1) \right) \right].$$

The important consequence of the transition to the continuum is the fact that the first two equations from (13) vanish from the calculation at $n_x \to z$, i.e. they are merged into the last of equations from (13), which in the continual approximation has the form:

$$d^2 A + \left[ E^0 - 4Q - \Phi (E - 4Q - 2W_z) \right] \left( \frac{2z}{L} \right)^2 A = 0 \quad (15)$$

By the assumption:

$$E > 4Q + 2W_z = E^{(0)}_{xyz},$$

and by the substitution:

$$\frac{2z}{L} - 1 = \tau \zeta, \quad \text{with} \quad \tau = \frac{W_x [a_z L]^2}{4Q (E - 4Q - 2W_z)},$$

the equation (15) becomes known Hermite-Weber equation:

$$\frac{d^2 A}{d\zeta^2} + (\kappa - \zeta^2) A = 0, \quad (16)$$

where $\kappa = \frac{L}{28z} \sqrt{Q (E - E^{(0)}_{xyz}) W_z}$. Here we introduce the requirement that the amplitudes $A$ are finite for arbitrary structure thickness (it means even for $L \to \infty$). For satisfying this requirement we must take known condition of the finiteness for the solutions for Hermite-Weber equation: $\kappa = 2\mu + 1; \quad \mu = 0, 1, 2, \ldots$ On the basis of this we find:

$$E_{\mu,2} = 4Q + 2b^2 (2\mu + 1)^4 \Phi W_z \left[ 1 \pm \left( 2\mu + 1 \right)^2 b^2 \Phi \right]^{-1/2}],$$

(17)

were $b = \bar{a}_z / L$. The expression for energies (17) indicates that index $\mu$ must be limited from below (the energies must be real):

$$2\mu \geq \frac{1}{b} \left( \frac{2}{b} \right)^{-1}. \quad (18)$$

It means that the mean allowed value of the index $\mu$ is the minimal integer which is bigger than
the final term in (19). As we can see, the lower boundary of quantum number \( \mu \) depends on the number of structural layers (through \( N_j \)), on the way of sputtering (through \( n_z \)) and on the type of ion-ion interaction (through \( h \)). If the thickness of the structure increases, the lower value of \( \mu \) increases too.

For simplifying, instead of the expression (19), we will use the approximate expressions for energies, which we obtain by the expansion of the square root up to the quadratic terms:

\[
E_1 = E_{xy}^{(0)} + 4b^2(2\mu + 1)^2\Phi W_z - \frac{W_z}{2(2\mu + 1)^2 b^2\Phi};
\]

\[
E_2 = E_{xy}^{(0)} + \frac{W_z}{2(2\mu + 1)^2 b^2\Phi}. \tag{19}
\]

It is very easy to notice that both obtained expressions for energies satisfy the necessary condition (18). However, by the analysis of (19), we can conclude the following.

- Since \( E_2 < E_1 \), the states with energy \( E_2 \) are more stable and more populated and so they essentially define the normal behavior of the system.

- From the expressions (19) it follows that the increase of film thickness (the increase of \( N_j \)) causes the increase of lower boundary of the index \( \mu \), and the correction of \( E_2 \), which depends on sputtering, decreases. This is in complete agreement with the conclusions which we can accomplish without going over to continuum, i.e. directly analyzing discrete equations (13).

We can see in expressions defining \( \zeta \), text under (18), that the boundaries of the interval for \( \zeta \) are proportional to \( L/2z = 1/b \) and so we can approximately take: \( \zeta = \left[-\infty, \infty\right] \), where the approximation is better if the film is thicker. We can then express the solutions of equation (16) using Hermits polynomials:

\[
A_\mu(\zeta) = \frac{e^{-\zeta^2/2}}{(2\mu)!\sqrt{\pi}} H_\mu(\zeta); \tag{20}
\]

\[
H_\mu(\zeta) = (-1)^\mu e^{\zeta^2/2} \frac{d^\mu}{d\zeta^\mu} (e^{-\zeta^2}); \quad \mu = 0, 1, 2, ... \]

In this way we have defined single-particle degenerate states of the system; for the wave functions – by the equations (11), (13) and (20) and for energies – by (19).

4. CONCLUSION

The particular features of high-temperature superconductors on the basis of oxide ceramics are their granular structure and the anisotropy of properties. The existence of the weak isotopic effect and Cooper pairs of charge carriers is experimentally verified, similar as in the conventional superconductors, but BCS model was not able to explain high critical temperature. For that reason and on the basis of established experimental results [16–20], we have proposed the model of ceramic structure as tetragonal i.e. generalized cubic structure in which interatomic distances along one direction are several times bigger than along the other two directions. It is, energetically, most convenient if the sputtered atoms locate themselves just along this direction.

The analysis of phonon spectrum in our model [21–25] yields that we have phonon branches of optical type only in the spectrum (there exists energy gap). It means that for phonon excitation it is necessary that the energy (heat) is bigger than the energy gap.

The analysis of electron spectrum in these symmetrically deformed structures (with respect to the planes \( n_z = 0 \) and \( n_z = N_j \)) yields that, as a consequence of existence of the boundaries along \( z \) axes, we have two energy branches in the spectrum of charge carriers. Lower value of energy is related to more populated states and contains the term depending on the sputtering. This term decreases with increasing of the film thickness. Higher value of energy in the spectrum of charge carriers is not particularly analyzed because these levels are low populated.

Acknowledgements

This paper was partly financed by the Ministry of Education, Sciences and Technological Development of the Republic of Serbia (Grand Nos. ON-171039 and TR-34019) and the Ministry of Science and Technology of the Republic of Srpska (Grant No: 19/6-020/961-23/14) as well as the Provincial Secretariat for Science and Technological Development of Vojvodina (Grant No: 114–451–927).

5. REFERENCES

IZVOD

MOGUĆA STANJA NOSILACA NAELEKTRISANJA U TANKIM VIŠESLOJNIM SUPERPROVODNIM KERAMIKA

U radu je analizirano ponašanje (spektri i stanja) elementarnih nosilaca n aelektrisanja u anizotropnim perovskitnim strukturama, kakve su savremene superprovodne keramike. Translaciona simetrija atomskih (jonskih) rasporeda sistema elektrona (ili šupljina) je narušena atomskim/jonskim/molekulskim rasproštanjem (spaterovanjem) i dopiranjem, kao i postojanjem dvegraničnih površina. Ovo je model nosilaca n aelektrisanja kod visoko-temperatskih superprovodnika u kojem se posmatrano našenje simetrije normalno na CuO ravni tretira kao perturbacija. Određene su jedno-ceštice fermionske talasne funkcije i moguće energije nosilaca naelektrisanja.

Ključne riječi: Nosioci naelektrisanja, granice, anizotropija, energetska stanja i spektri, jedno-ceštice talasne funkcije.

Naučni rad
Rad primljen: 09. 02. 2016.
Rad prihvaćen: 24. 03. 2016.
Rad je dostupan na sajtu: www.idk.org.rs/casopis