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THEORETICAL POSSIBILITY OF INCREASING OF SUPERCONDUCTIVITY TRANSITION TEMPERATURE IN HIGH TEMPERATURE SUPERCONDUCTORS BY REPLACING OXYGEN WITH CHALCOGEN

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The paper discusses the experimental data that evidence the increase of the critical temperature of superconductivity in Y-Ba-Cu-O system, when doped with chalcogens.

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1. Introduction

In the present paper the experimental data which evidence of increasing of superconductivity transition temperature (T_c) in high-temperature superconductor of YBaCuO system doped with chalcogenides have been discussed. The interpretation of experimental data has been done in the frame of the negative-U centers model. The opportunity of changing and, probably, increasing of temperature of superconducting transition in materials such as YBaCuO by replacement of atoms of oxygen by atoms of chalcogenides is considered. It is supposed that if someone could replace large amount of oxygen with chalcogenides (for example sulfur) the significant increasing of T_c can be obtained.

2. Theoretical model and calculations

The $Y_1Ba_2Cu_3O_7$ material is the high-temperature superconductor, its temperature of transition is equal to ≈90K. As it is known, the standard theory BCS [1], describing superconducting transition in metals, explains processes in high-temperature superconductors (HTSC) not very well. So for example, the temperature of transition in BCS is described by the formula

$$T_c=1{,}14\cdot\hbar\cdot\omega_d\cdot\exp(-1/g\cdot\nu) \quad (1)$$

Where g is a constant of electron-lattice interactions, ν – density of electron states at Fermi level and ω_d – characteristic frequency. If we describe high-temperature superconducting transition with this formula then we obtain T_c approximately twice less than experimental value. Nowadays many alternative models are created for the HTSC description. The present approach are based on concepts of the model of the localized pairs of electrons [2] and negative-U center model [3]. In these models electronic pairs, in contrast to BCS theory, exist already at T > Tc. Using the model [2], it is possible to show how T_c is changing with change of the matrix element of a electron transition from one center of localization to another. It will be shown that adding of chalcogenides into superconductor under studding increases T_c. This statement proves to be true by experiments [4].

The given model is described by Hubbard Hamiltonian

$$H=-U\cdot\sum n_{i\uparrow}\cdot n_{i\downarrow}+\sum t_{ij}\cdot a_{i\sigma}^{+}\cdot a_{j\sigma} \quad (2)$$

Where $n_{i\sigma} = a_{i\sigma}^{+} \cdot a_{i\sigma}$ are occupation numbers, $a_{i\sigma}^{+}$ and $a_{i\sigma}$ are operators creating and annihilating electrons with spin σ on center i, and t_{ij} – matrix element of transition between the nearest centers of localization (negative-U centers). It is considered that U > 0 and $t_{ij} << U$. Negative values of -U lead to attraction between electrons with opposite spins on the same negative-U center. At low temperatures Hamiltonian (2) leads to occurrence of superconducting correlation between electron pairs. The second term of Hamiltonian (2) corresponds to kinetic energy of band movement (width of an one electron band $\approx |t_{ij}|$), and the first - to interaction between electrons with energy U. In the BCS model the width of the band is great, and consequently interaction is examined as perturbation. The main difference of investigated model from the BCS model is that the width of the band is considered small in comparison with U, so the second term of Hamiltonian (2) is examined as perturbation.

At T=0 all electrons are in the pairs localized on the negative-U centers. At $T \neq 0$ system represents assembly of empty centers, the centers occupied with one electron, and the centers occupied with two

electrons. Number of negative-U centers occupied with one electron is proportional to $n \cdot \exp(-U/T)$, where n is concentration of electrons. When **T** << U, amount of single electrons is a very little in comparison with number of pairs, then concentration of single electrons can be neglected. In this case, solving the Hamiltonian (2), we are obtaining the formula (3) for temperature of superconducting transition [2].

$$T_c = W \cdot (1-2\nu)/\ln(\nu^{-1}-1) \quad (3)$$

Where $W=2zt^2/U$ – width of the pairs band, z – number of the nearest neighbors of the given center, ν – relative concentration of electronic pairs ($\nu = n/2 \cdot N$, N – concentration of negative-U centers).

As it is described in the paper [3] electron-lattice interaction results in negative correlation energy that intrinsic defects (D), being negative-U centers, get a various charge ($D^{+,0,-}$). Strong interaction of two electrons results in that the reaction $2D^0 \rightarrow D^+ + D^-$ becomes exothermic. Such reactions may occur in superconductors YBaCuO, they are fair for atoms of copper and run under the following circuit (4)

$$2Cu^{2+} \rightarrow Cu^{3+} + Cu^{+} \quad (4)$$

Presence of ions $Cu^{3+,2+,1+}$ was confirmed experimentally [5]. From the statistical point of view reaction (4) means that ions of copper is spending equal time in Cu^{3+} and Cu^{+} states, exchanging charges with neighbors. It is assumed and proved in [3], that $Cu^{3+,2+,1+}$ states may be considered as $D^{+,0,-}$ states of the negative-U centers. This allows us to count, that ions Cu in lattice YBaCuO (Fig. 1) are the negative-U centers.

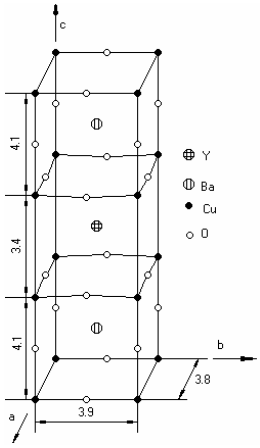

Fig. 1. Structural lattice of $Y_1Ba_2Cu_3O_7$.

Analyzing the formula (3) it is easy to see, that for increasing of the T_c it is necessary to increase t which is a matrix element of electron transition from one negative-U center to another. In structural lattice these centers are separated from each other by oxygen (Cu-O-Cu, direction b), so it is necessary to examine interaction between copper and oxygen. It is needed because a direct matrix element of electron transition from one atom of copper to another (distance between them is 3,9Å) is several times less than the matrix element calculated for atoms Cu and O on distance 1,95Å. The matrix element of this transition will be approximately estimated in two-nuclear molecule CuO.

Possible way of increasing t is replacement of atoms of oxygen by elements of the same group. We examine the sulfur. For calculations of the matrix elements of electron transition from the copper ion to the ion of oxygen or sulfur (6) the electronic functions (5) entered by Slater [6] were used.

$$\begin{aligned} &Cu\ (3d\text{-state})\ \Psi_{Cu} = (x^2-y^2) \cdot \exp(-cCu \cdot r/3) \\ &O\ (2p\text{-state})\ \Psi_O = x \cdot \exp(-cO \cdot r/2) \\ &S\ (3p\text{-state})\ \Psi_S = x \cdot r \cdot \exp(-cS \cdot r/3) \end{aligned} \quad (5)$$

Where cCu, cO, cS is the effective shielded charges for the given elements.

$$\begin{aligned} t_{CuO} &= \int \Psi_{Cu}(r) \cdot H(\Psi_O(r-R))dV \\ t_{CuS} &= \int \Psi_{Cu}(r) \cdot H(\Psi_S(r-R))dV \end{aligned} \quad (6)$$

Where R is a distance between atoms, $H = -\nabla^2 - \frac{cCu}{r_1} - \frac{cO}{r_2}$, cO in the second integral (6) is replaced by cS. Matrix elements of transition t_{CuO} and t_{CuS} are showing how transition of electron changes in process of atoms removal from each other (Fig. 2). From Fig. 2 it is seen (distance more than 1,5Å) that realization of a situation when the matrix element t_{CuS} for sulfur will be greater, than t_{CuO} for oxygen, can be obtained. Even a small difference of inter-nuclear distances in bonds CuO and CuS leads to significant difference in values t_{CuO} and t_{CuS}. For example, in the lattice $Y_1Ba_2Cu_3O_7$ distance between atoms Cu and

O 1.95Å, so t_{CuO} is equal -0.609 Ry. If in the same structural lattice we replace some of atoms of oxygen by atoms of sulfur we should gain some increase of T_c, because the matrix element of transition Cu-S on distance 1.95Å is equal -0.929 Ry. In the ideal case the transition temperature (if all atoms would be replaced) would be increased by 2.3 times. But it is not known constants of a structural lattice for full replacement of atoms O by atoms S. If the constant b of the lattice will decrease, that was shown in experiments [4], both t_{CuO} and t_{CuS} significantly would increase, so T_c would be increased sharply. If inter-nuclear distances will increase (this conclusion is possible, comparing molecules CuO and CuS), T_c will exceed 90K up to some critical distance equal 2,26 Å because t_{CuS} is more than t_{CuO}. In Table 1 matrix elements of transition values of examined atoms in various bonds are shown. These data shows that in simple bonds absolute value t_{CuS} normally exceeds t_{CuO}. As we expect, in HTSC will be maintained the same tendency, and T_c will increase in the case of sulfur addition.

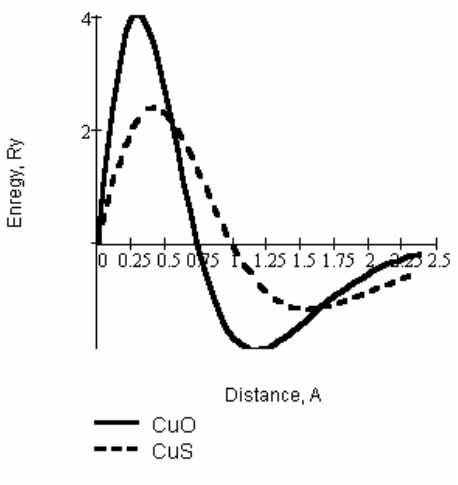

Fig. 2. Dependence of matrix element of electron transition from ion Cu to

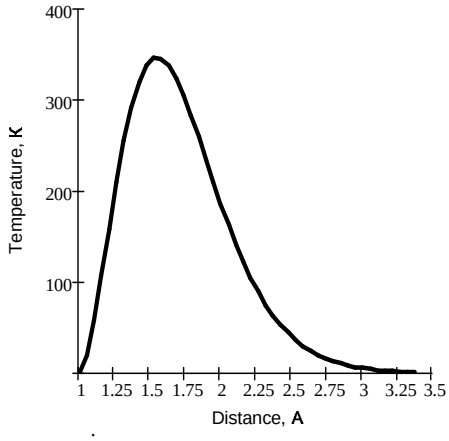

Fig. 3. Dependence of temperature of superconducting transition on distance between ions Cu and S in the structure YBaCuS.

3. Discussion of experimental dat

The results confirming our assumption have been obtained in the paper [4]. In this paper the small amount of sulfur or selenium was added in structural lattice $Y_1Ba_2Cu_3O_7$, thus the temperature of superconducting transition was increased, and constants of structural lattice were changed (tab. 2). Apparently, additions even a small number of chalcogenides caused substantial increasing of temperature. Reduction of the average inter-nuclear parameter b is probably caused by local increasing of distances between atoms of copper and sulfur in comparison with distances between copper and oxygen. Therefore, a lattice relaxed distances between copper and oxygen have slightly decreased, in comparison with that case where chalcogenides is not present. However it is not necessary to reject variant when the distances between atoms of the given direction have decreased in comparison with initial structure everywhere, including atoms Cu and S.

Table 1. Temperature of superconducting transition depending on values of matrix element of transition at various distances between atoms Cu and O, Cu and S.

Structure	Distance (b) between atoms Cu and O (S)	t, Ry	T_c (t), K
$Y_1Ba_2Cu_3O_7$	1.95Å	-0.609	90
CuO	1.95Å	-0.609	90
CuS (0)	1.95Å	-0.929	209
CuS (1)	2.19Å	-0.680	112
CuS (2)	2.32Å	-0.556	75

In this case, apparently from Fig. 2, it is possible to expect for distances less than 1.95 Å substantial growth of the T_c because of atoms Cu and S, Cu and O have approached to each other and the matrix element of transition *t* have grown.

Table 2. Experimental data of temperature's of superconducting transition changing in case of addition of chalcogenide elements in YBaCuO [4].

Structure	T_c	ΔT	a, Å	b, Å	c, Å
$Y_1Ba_2Cu_3O_{7-x}$	89.5K	0K	3.83	3.89	11.68
$Y_1Ba_2Cu_3O_{7-x}S_{0.001}$	90.5K	1K	3.83	3.87	11.67
$Y_1Ba_2Cu_3O_{7-x}S_{0.05}$	93K	3.5K	3.84	3.87	11.62
$Y_1Ba_2Cu_3O_{7-x}Se_{0.5}$	91K	1.5K			

We consider a case when only 0.05 amount of sulfur (Table 2) was added to original structure and the inter-nuclear parameter b has decreased on 0.02Å. It is possible to make a conclusion, that distances between ions Cu and O have approximately changed by 0.01Å. Then it is possible to estimate how the temperature will increase depending on change of the matrix element t_{CuO}. The t_{CuS} can be not taken into calculation, because it is much less atoms of sulfur than atoms of oxygen in this new structure.

$$T_c^1 = \left(\frac{t_{CuO}(1.94A)}{t_{CuO}(1.95A)} \right)^2 \cdot 89.5K = 93.7K \qquad (7)$$

As it's seen from the formula (7) temperature obtained theoretically coincides rather well with experimental one, which is equal 93 K. Fig. 3 represents dependence T_c on distance between Cu and S calculated by the formula the same as (7). In this case it is considered, that all atoms of oxygen are replaced with atoms of sulfur. It is clearly visible from this diagram that the temperature sharply grows with reduction of inter-nuclear distances. The peak is observed in area near 1.6-1.7Å that corresponds to changing of a constant *b/2* only by 0.3Å. For all *b/2*<2.2Å the exceeding of temperature is possible.

4. Conclusions

Clearly, that practically achievement of such temperatures, as 350K (the maximal value on Fig. 3) by the method described in the given work, most likely is impossible. First of all in the given work only approximate calculations for estimation of T_c were used. However the tendency to increasing of temperature is seen rather clearly and it has proved to be true and in practice.

We shall note two possible variants of increasing Tc, when sulfur are added to YBaCuO, based on fact that the temperature of transition is proportional to the quadrant of matrix element of transition *t*.

· the inter-nuclear parameter *b* is increased. The temperature of transition grows because the matrix element of transition t_{CuS} (distances between ions Cu and S is less than 2.26Å) will exceed t_{CuO} for ions Cu and O in original structure.

· the inter-nuclear parameter *b* decreases. Both t_{CuS} and t_{CuO} are increased, therefore, even if full replacement of oxygen by sulfur is incomplete, strong increase Tc is expecting.

It is necessary to note, that creating of new structures is very difficult, because method used for creating usual HTSC is hard to apply for new materials. For example, addition in YBaCuO large concentration of S or Se lead to appearance of a new dielectric phase, and the samples lose the superconducting properties and become isolator.

We think that it is possible to rely on the model of the negative-U centers, which qualify coincides with experiments [4]. If estimation of T_c, which was calculated using of this model, is true, creating of superconductors with temperature of transition more than 110K is possible.

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