APPLICATION OF CHALCOGENIDES FOR CREATION OF NEW SUPERCONDUCTORS

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There was shown that some properties of both glassy semiconducting chalcogenides and HTSC cuprates can be explained in the frame of negative-U center model. This can lead to creation of new superconducting materials with improved properties based on chalcogens and HTSC cuprates.

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1. Introduction

Presently, there are no logically complete and consistent theories of superconductivity in chalcogenide glassy semiconductors (CGS) and high-temperature superconductivity in cuprate systems (HTSC cuprates). There are many points of view on the nature of high-temperature superconductivity (HTSC). Some authors believe that modified classic Bardeen-Cooper-Schrieffer model can be adopted for the explanation of HTSC [1], others develop totally new theory of electrons attraction, for example, due to appearance of negative effective mass [2]. Several years ago we put forward for explaining HTSC negative-U center model of superconductivity (NUCS model). This model allows us to explain the origin of superconductivity in cuprates and chalcogenides and also to compare the characteristics for these materials. In the framework of this model it is possible to describe many others properties, such as pinning of Fermi level and appearance of pseudo-gap in the normal state of HTSC cuprates. It is shown that chalcogenides and HTSC cuprates have similar properties including superconductivity because there are special structural units called negative-U centers in these materials [3, 4]. Some experiments show that even unified coherent state can occur in mixture of chalcogenides (Se) and HTSC cuprates (YBaCuO) which lead to superconductivity [5]. In [6,7] the possible superconductivity in chalcogenide glasses is discussed theoretically.

This paper is devoted to the possibility to create a new superconductor system based on HTSC cuprates in which we propose to replace the oxygen with chalcogens, particularly sulfur and possibly selenium.

2. Conception of negative-U centers

It is very well known that there is a large concentration of intrinsic defects in chalcogenides, which makes impossible to dope these materials: Fermi level is staying in the middle of band-gap while the concentration of impurity is less than that of defects (Fig. 1) [8]. This property is called pinning of the Fermi level and defects are called negative-U centers. It is profitable for two electrons to attract at a defect site and form a pair, because of negative energy of electron interaction [3]. That is why the name “negative-U center” was proposed.

It is very possible that negative-U centers also exist in high temperature superconductors (such as YBaCuO, PrBaCuO). This has been confirmed by experiments, which showed that in these
materials copper exists in different charge states Cu$^{+1}$, Cu$^{+2}$, Cu$^{+3}$, which correspond to the charge states of negative-U centers: D$^-$ (there are two bounded electrons on one center), D$^0$ (center in the neutral state, with one native electron), D$^+$ (there are two bounded holes on the center). The appropriate band diagram for YBaCuO is shown in Fig. 2. The possible atomic configurations, which may play the role of negative-U centers in a-Se and YBaCuO, are presented in Fig. 3 and Fig. 4, respectively.

![Band Diagram](image)

Fig. 1. Band energy diagram of a-Se. The vertical arrow shows the thermal transition of holes to the D$^-$ state of the negative-U center. Shaded bands represent the bands of non-localized electron and hole pairs (D$^-$ and D$^+$ bands of bosons), whose Bose condensation is responsible for the superconductivity.

![Band Diagram](image)

Fig. 2. Band diagram of Y$_2$Ba$_2$Cu$_3$O$_x$. D$^+$ and D$^-$ are bands of negative-U centers and they are shaded. $E_f$ is slightly higher (about 100 meV) than the top of the valence band. $E_{1,2}$ are the first and the second energy activation of negative-U center.

![Structure Diagram](image)

Fig. 3. Simplified structure of a-Se with two negative-U centers. The first center D$^+$ is located at the position 1 and the second center D$^-$ is located at the position 2 (a). The two centers are equivalent and they can exchange by two electrons – then they may change places (b).

![Lattice Diagram](image)

Fig. 4. Lattice of Y$_2$Ba$_2$Cu$_3$O$_x$. Atom of copper can be the main part of negative-U center. Existence of oxygen defines properties of Cu, so negative-U centers are not only atoms of cuprum but their oxygen surroundings are also included.

Early developed theory predicted the appearance of superconductivity in the system consisting of negative-U centers [9]. The results of this theory have been used for elaboration of the NUCS model and explaining of superconductivity in the YBaCuO system [4].

The model of negative-U centers allows to explain many properties of this type of superconductors, such as: high value of temperature of superconducting transition $T_c$, dome-shaped $T_c$
dependence on doping YBaCuO with oxygen, appearance of the pseudo-gap, changing of conductivity from metal like to semiconductor like for different temperatures [10].

The very presence of negative-U centers in HTSC leads to unusual properties of these materials. Because of reaction (1), which is exothermic, two neutral negative-U centers are exchanging the charges, so there are boson consisting of two bounded electrons on one center (D') and boson consisting of two bounded holes on another (D'').

\[
2D^0 \rightarrow D^+ + D^-
\]

\[
2E(D') = E(D') + E(D'') + U
\] (1)

The energy of bounding U is so high, that bounded electrons exist as pairs at temperature higher than several hundreds Kelvins. Because the pairing of electrons already happens at temperature much higher than \(T_c\), only pairs condensation in coherent state at \(T_c\) takes place, which leads to superconductivity. The value of \(T_c\) may be calculated by formula (2) [9]:

\[
T_c = \frac{W}{\gamma} (1 - 2\gamma) / \ln(\gamma^{-1})
\] (2)

Where \(W = 2\gamma^2/U\) – width of the pairs band, \(\gamma\) – number of the nearest neighbors of the given center, \(\nu\) – relative concentration of electronic pairs (\(\nu = n/2N\), \(N\) – concentration of negative-U centers, \(n\) – electron concentration) and \(t\) – matrix element of electron’s transition from one negative-U center to the nearest one.

3. Similar properties of chalcogenides and HTSC cuprates

3.1 Pinning of Fermi level

The very presence of negative-U centers in chalcogenides and HTSC leads to a series of similar properties in these materials. It is known that chalcogenides behave as intrinsic semiconductor independently on extrinsic doping because Fermi level is pinned at the middle of the band-gap by negative-U centers. We suppose that in high temperature superconductors the energy bands of negative-U centers are situated in such position that Fermi level is pinned slightly higher than the top of the valence band (Fig. 2). Such location of energy levels and bands leads to very low activation energy of electrons from the valence band. So HTSC behaves like metal at near-room temperature, but they become hole semiconductors at the temperature comparable to \(T_c\) (particularly it is very well
emphasized for underdoped samples). Calculation made in the frame of negative-U center model confirms this assumption about relative position of Fermi level, bands of negative-U centers and valence and conduction bands (Fig. 5).

3.2 Temperature dependences of resistance and $T_c$.

It is known that the properties of chalcogenides and HTSC change dramatically with applied pressure [10, 11]. Firstly, the resistance of materials is dropping with increasing pressure. Secondly, superconductivity appears in chalcogenides at high pressure and temperature of superconducting transition increase with pressure rising (Fig. 6). In PrBaCuO superconducting transition exists without pressure, but temperature $T_c$ rises with pressure also.

Fig. 7. Experimental temperature dependence of resistance of a-Ge$_{33}$As$_{12}$Se$_{35}$ for different pressure. Pressure, kbar: 1 – 170, 2 – 173, 3 – 178, 4 – 183, 5 – 190, 6 – 200, 7 – 218 [12].

Fig. 8. Temperature dependence of resistance of PrBa$_2$Cu$_3$O$_{6.6}$ for different pressure. Big dots are experimental data [13], thin lines are theoretical values.

Fig. 9. Pressure dependence of superconducting transition temperature and activation energy for a-As$_2$Te$_3$[12].

Fig. 10. Pressure dependence of superconducting transition temperature and activation energy for PrBa$_2$Cu$_3$O$_{6.6}$ [13].

The resistance's decrease under pressure may be explained by decreasing of forbidden gap as in the case of CGS (Fig. 7) or of energy gap between the top of valence band and Fermi level, as for HTSC (Fig. 8). In both cases the increase of concentration of negative-U centers may play a significant role. In the present paper the calculation has been done by the scheme used in [10] and it
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shows fine agreement of theoretical and experimental data (Fig. 8). Regarding the superconducting transition the situation is rather different. In chalcogenides the superconductivity appears only under pressure of magnitude by several kbar and \( T_c \) does not raises usually higher than ten kelvins (Fig. 9). In HTSC superconductivity exists without applied pressure and temperature of its appearance is about hundred Kelvins (Fig. 10). The difference between these materials can be explained in the following way: in HTSC negative-U centers are atoms of lattice, their concentration can be equal to \( 10^{20}-10^{21} \) cm\(^{-3}\), in chalcogenides negative-U centers are defects with concentration about \( 10^{17}-10^{18} \) cm\(^{-3}\). It is obvious that at normal conditions in CGS there is insufficiently large concentration of centers with electron pairs for creation of a superconducting cluster in whole volume of the material. This concentration rises under pressure (probably because of the appearance of new defects). When it reaches a critical value then a percolation superconducting current is possible. Also, it is important both for HTSC and chalcogenides that the matrix element \( t \) is rising under pressure because of decreasing lattice constants. Due to this matrix element \( t \) the exchange of charge carriers between neighboring negative-U centers occurs. Superconducting transition temperature increases quadratically when \( t \) increases, as seen from formula (2).


As it has been shown in [14] the matrix element \( t \) can be modified by changing distance between negative-U centers. This can be done not only by pressure, but also by replacing atoms of oxygen, which respond for charge exchange between negative-U centers in HTSC cuprates, by atoms with similar properties, in particular by sulfur or selenium. In this case not only lattice constants are changing, but also copper-chalcogen and copper-oxygen interactions change. This occurs mainly because the atomic radii of chalcogens are significantly larger than the radius of oxygen. The matrix elements of Cu-O and Cu-S transitions depend on distance between atoms and are shown on Fig. 11. The calculation has been made by using the approximation of diatomic molecule [14].

Taken into account this calculation and that \( T_c \) depends quadratically on \( t \), the superconducting transition temperature in the new compound YBaCuS can be estimated using the formula (3):

\[
T_c(YBaCuS) = \left( \frac{t_{CuS}(\lambda)}{t_{CuO}(I,95,A)} \right)^2 \cdot T_c(YBaCuO)
\]  (3)

Fig. 11. The matrix element of electron transition from Cu to O and from Cu to S as a function of the distance between ions.

Fig. 12. Dependence of superconducting transition temperature on distance between ions Cu and S in the structure YBaCuS.
As it is seen from Fig. 12, if the distance between elements of copper and sulfur in the new compound will be greater than 1.4 Å and less than 2.2 Å then the superconducting transition temperature would rise (if the remaining parameters stay unchanged). It is also possible that if oxygen is not completely replaced by sulfur then this can also lead to a slight increase of \( T_c \).

Slightly increase of superconducting transition temperature because of changed lattice parameters was proved by experiments, when small amount of sulfur was introduced in YBaCuO [15]. As it is seen from Table 1, changing of the lattice constants by 0.01 Å can lead to the increase rising of transition temperature by 2-3 degrees. Theoretically calculated \( T_c \) are in close agreement with experimentally ones.

Table 1. Experimental data [15] and theoretical calculation of superconducting transition temperature changing in case of addition of chalcogen elements in YBaCuO.

<table>
<thead>
<tr>
<th>Structure</th>
<th>( T_c )</th>
<th>( \Delta T )</th>
<th>( T_c ) theory</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_1Ba_2Cu_3O_{7-x} )</td>
<td>89.5K</td>
<td>0K</td>
<td>89.5K</td>
<td>3.83</td>
<td>3.89</td>
<td>11.68</td>
</tr>
<tr>
<td>( Y_1Ba_2Cu_3O_{7-x}S_{0.001} )</td>
<td>90.5K</td>
<td>1K</td>
<td>91.9K</td>
<td>3.83</td>
<td>3.87</td>
<td>11.67</td>
</tr>
<tr>
<td>( Y_1Ba_2Cu_3O_{7-x}S_{0.05} )</td>
<td>93K</td>
<td>3.5K</td>
<td>93.7K</td>
<td>3.84</td>
<td>3.87</td>
<td>11.62</td>
</tr>
<tr>
<td>( Y_1Ba_2Cu_3O_{7-x}Se_{0.15} )</td>
<td>91K</td>
<td>1.5K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The authors of the paper [15] could not prepare samples with significant amount of sulfur and selenium by direct synthesis. The phase separation has occurred and a non-homogeneous mixture was obtained.

Here we would like to suggest a modified technique, which, allows to prevent phase separation in the case of significant amount of dopants for the chalcogenide glassy semiconductors [16,17]. We hope that this technique will be useful for preparing homogeneous, may be non-crystalline HTSC films, with significant amount of S and Se and increased value of \( T_c \).

5. Conclusion

The model of negative-U center for the superconductivity property, developed in this paper shows that the MTSC cuprates and chalcogenide glasses have many similarities, including the origin of superconductivity.

References