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POSSIBLE HIGH TEMPERATURE SUPERCONDUCTIVITY IN CHALCOGENIDE GLASSY SEMICONDUCTORS

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High T_c superconductivity in composite system of selenium matrix with globular Y-Ba-Cu-O is discussed in relation to the experimental results.

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1. Introduction

In our recent paper [1] we have elaborated the model of superconductivity, which may be realized in the system of negative – U centers with a large concentration. The model is based on the theoretical results of paper [2]. It is supposed in [1], that manifestation of negative – U centers model of superconductivity (NUCS – model) may be found in chalcogenide glassy semiconductors, because these substances are known as matters with a large concentration of negative – U centers. Then in the present paper we discuss several experimental results, which might confirm our hypothesis.

2. Analysis of experimental data

The present paper is devoted to investigation of superconductivity of the samples, which consist of globules of well known high temperature superconductor (HTSC) with $Y_1Ba_2Cu_3O_7$ composition which are embedded in glassy Se matrix. The details of samples preparation have been described in [1], and here we briefly remind the most important ones only. A little bubble (volume ~ 1 mm^3) of a-Se mixture with micro-crystalline pieces of $Y_1Ba_2Cu_3O_7$ (or globules) are located between two intersecting wolfram wires. Diameters of wires are equal to 50 μm. The bubble has been melted by Joule heating of wolfram wires, melting substance entered between wires and separated them at distance L. Micro-crystalline pieces of $Y_1Ba_2Cu_3O_7$ – globules- have linear size about several micrometers and occupy approximately 14% of whole volume then all of them have been separated by a-Se. Two sets of samples have been investigated.

The first set consists of low-resistance samples with resistance R at room temperature of order R~1 Ω. This value can be estimated from date of Fig. 1a (curve 1). The distance L between electrodes for these samples has a minimum value L~1 micrometer and so L is less than linear size of globules one can conclude that there are several globules which join two contacts. This conclusion may be confirmed by estimation of the conductivity value $\sigma \sim L/RS$. One can obtain for typical square of globule cross-section S ~10 μm^2 the conductivity value of order ~$10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$, which rather well coincides with the conductivity of $Y_1Ba_2Cu_3O_7$ at room temperature. The superconductivity phase transition temperature T_c for these samples approximately coincides with that one for $Y_1Ba_2Cu_3O_7$ ($T_c \approx 90$ K) [1]. The value of critical current density, which can be estimated from the initial current jump of curve 2 (Fig. 1a) at U=0, equals to ~ 2 A/cm^2 and coincides with known value for HTSC [2].

Then one can conclude, that electrical properties of of low-resistance samples at all temperatures: $T>T_c$ and $T<T_c$ are governed by HTSC.

The second set consists of high-resistance samples with R~10^4 Ω at room temperature (see Fig. 1b, curve 1). The typical distribution of HTSC globules through the sample cross-section obtained by X-ray microanalysis is shown on Fig. 2, which is taken from paper [1]. It is very well seen, that globules are separated and there is not the continuous current path trough them. Solid line has been depicted by authors to show the possible current path through the several globules and a-Se inter-globule layers. The total effective thickness of these layers may be taken as ~10 μm. The distance between electrodes for these samples has a value more than for the low-resistance samples and one can use for estimation the value L~50 μm. If one takes the linear dimension of globule ~5 μm as the diameter of current path cross-section then the conductivity value of order ~10^{-6} Ω^{-1} cm^{-1} may be obtained at room temperature. This value very differs from the value ~10^{-12} Ω^{-1} cm^{-1} for pure a-Se. It is known that conductivity of a-Se very depends on the doping with oxygen [3], then we can suppose that a-Se channels, which join globules and are depicted by solid line (Fig. 2) consist of glassy selenium doped with oxygen catched from air or from globules.

But we would like to emphasize that in any case the resistance of high-resistance samples at room temperature ($T>T_c$) is not controlled by HTSC.

Phase transition temperature T_c for samples from the second set is the same as for $Y_1Ba_2Cu_3O_7$ [1] and one can see the direct superconducting current through whole sample, which existence at U=0 and T=77 K(Fig 1b, curve 2). Hence a conclusion was made in [1] that Josephson contacts are formed between HTSC globules embedded in the a-Se matrix, making possible the superconducting transport in these samples.

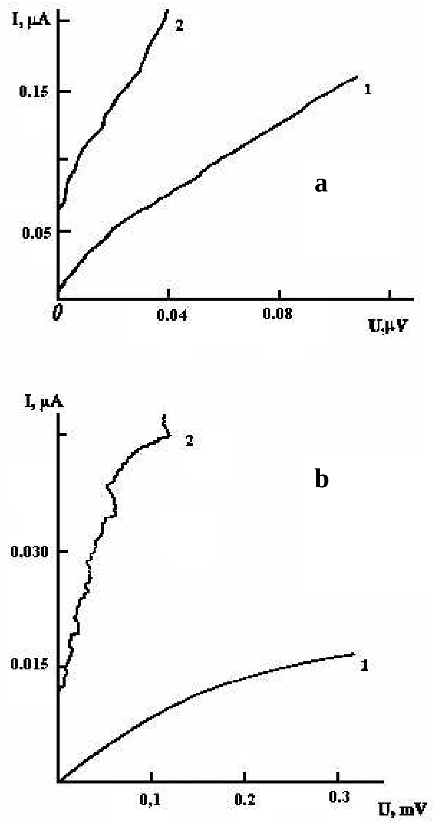

Fig. 1. I-V characteristics of (a) low- and (b) high-resistance samples at temperatures T = 297 (1) and 77 K (2).

The most important fact we would like to emphasize in present paper consists in the following. It is known presently that the correlation length ξ in HTSC materials is small and equals to 10-15 Å [4, 5]. Consequently, the thickness of the Josephson contacts must be of the same order of magnitude. At the same time, it can be seen from Fig. 2 that the a-Se spaces between HTSC globules have linear dimensions of several micrometers, i.e. 10^3 times ξ. Hence follows that the superconducting properties of the sample as a whole can only be accounted for under the assumption that a-Se in spaces between the globules also would possesses superconducting properties with T_c not lower than that of $Y_1Ba_2Cu_3O_7$. This assumption does not refer to the entire volume of selenium known not to exhibit high-temperature superconductivity. We mean here only the channels appearing between the HTSC globules in electric field as a result of switching, shown schematically, as the guide to the eye, by the solid broken line in Fig. 2. It is known that the transition of a thin Se layer from the state with high resistance to that with low resistance (switching effect) occurs in an electric field with strength on the order of 10^5-10^6 V/cm [6]. At the same time, the external field strength in [1] did not exceed 10^2 V/cm, even with the effective thickness of the a-Se layer taken to be ~0.1 μm. Thus, it can be assumed that a-Se presents between HTSC globules has unusual properties and is switched in weak external electric fields or there are strong internal electric field in the vicinity of HTSC – a-Se boundary.

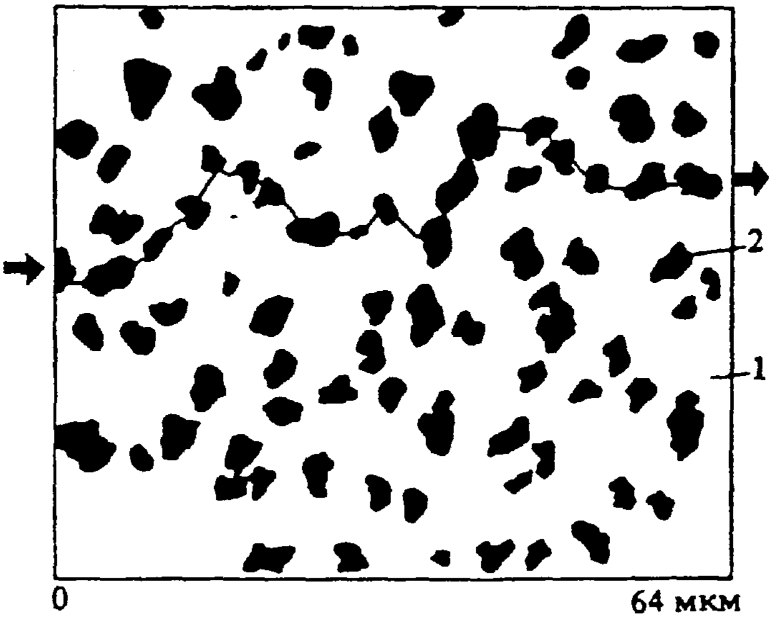

Fig. 2. Distribution of elements over the sample cross-section, obtained by means of X-ray microanalysis (reproduced from [1]). (1) Selenium and (2) HTSC. The solid, broken line showing the path of the through current represents a set of superconducting Se channels connecting adjacent HTSC globules.

It is for channels of this kind, appearing as a result of switching in chalcogenide glassy semiconductors (CGS), whose representative Se is, that a model of superconductivity has been proposed recently [7], based on the concept of centers having negative effective electron correlation energy U (negative-Ucenters). At present, it can be considered a well-established fact that it is the negative-U centers that are the predominant type of native defects in chalcogenide glassy semiconductors. For the reason of negative U, electrons (holes) are effectively attracted when residing on a defect and thus form pairs of electrons or holes, which are bosons. It was assumed in [7] that, at a sufficiently high concentration of negative-U centers, their states may form bands of delocalized pairs of electrons or holes, whose Bose condensation gives rise to superconductivity. Just the simplest CGS - glassy Se, was considered in [7] as an example. Fig. 3 shows schematically the band of electron and hole pairs: D(-) and D(+) bands made of non-superconducting metals exists only in strong electric fields. The parameters of negative-U centers in a-Se can be found from drift mobility measurements. The thermal activation energy of hole drift in the valence band is 0.14 eV [3], which corresponds to capture of holes into states of the electron pair. Therefore, it can be assumed that the center of the D(-) band lies 0.14 eV above the top of the a-Se valence band. The same figure shows the expected energy of optical ionization of the D(-) states, which, according to a simple theory of negative-U centers, must be twice the thermal ionization energy.

Thus, the Bose condensation of delocalized electron pairs in the D(-) band arising from the

D(-) level may be thought of as being responsible for the superconducting properties of the selenium channel connecting HTSC globules. It was believed in [7] that the superconducting channel appearing upon switching in CGS samples with electrodes

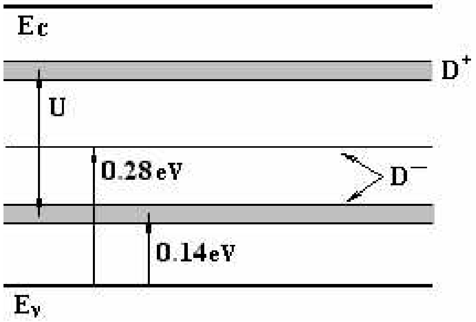

Fig. 3. Band energy diagram of a- Se. The arrows show the thermal and optical transitions of holes to the D¯ states of the negative-U center. Two dark bands present the bands of delocalized electron pairs - D¯ and D^+ bands, whose Bose condensation is responsible for the superconductivity.

By contrast, in the case in question, it should be considered that the channels between the HTSC globules arise in samples prepared from a mixture of HTSC and a-Se already on applying a weak measuring field. This distinction suggests that the role played by globules located at the channel ends consists in reducing the field strength necessary for superconductivity to appear in the a-Se channel. A large number of negative-U centers may exist in the channel due to self-compensation processes induced by doping with oxygen [8]. Additional concentration of negative-U centers arise during the switching effect in the internal electric field or in the weak external electric field which is used for current observation. The superconductivity in the system of negative-U centers in the channel may be induced by superconductivity phase transition in micro-crystalline pieces of $Y_1Ba_2Cu_3O_7$ which occupy two end of each channel. It was suggested in [7] that a situation similar to that observed in CGS may arise in organic polymers in which negative-U centers also, possibly, exist. The results of recent studies [9, 10] confirm this assumption. In these investigations, as also in the present study, the superconducting state was observed in channels of organic polymers connecting electrodes made of superconducting metals.

3. Conclusion

The experimental evidences of possible high temperature superconductivity in chalcogenide glassy semiconductor Se have been revealed and discussed for samples which consist of globules of well known HTSC with $Y_1Ba_2Cu_3O_7$ composition which are embedded in glassy Se matrix. The superconductivity possibly takes place in Se channels with linear dimension of several microns which arise between $Y_1Ba_2Cu_3O_7$ globules due to may be switching effect. The parameters of channels determined for normal and superconductivity states have been described by negative-U centers model rather well.

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