

SUPERCONDUCTIVITY IN CHALCOGENIDE GLASSY SEMICONDUCTORS

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The role played by the lone-pair electrons on the superconductivity of chalcogenide glasses is discussed. It is suggested that many specific features of superconductivity in chalcogenide glasses are due to the superconductivity of a system of negative-U centres, rather than to the BCS nature of the phenomenon.

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1. Introduction

The physics of Chalcogenide Glassy Semiconductors has already existed for about 50 years. During this entire period, the name of Stanford R. Ovshinsky has been associated with landmark contributions to science and technology of Chalcogenide Glassy Semiconductors. All of us remember the important role of the famous paper in Physical Review Letters (1968) [1], which was devoted to the switching effect. This paper has promoted intensive investigations of Chalcogenide Glassy Semiconductors in different countries all over the world. Chalcogenide Glassy Semiconductors were discovered in our institute by B. T. Kolomiets and N. A. Gorunova [2,3] and were investigated at the laboratory headed by B. T. Kolomiets. The paper [1] gave new powerful impetus to these investigations. This paper also changed my life dramatically, because, according to a special decision of our Academy of Sciences, it became possible for me and other young scientists to join the A. F. Ioffe Physico-Technical Institute staff. Our task was to investigate the switching and memory effects, and I would like to express my sincere gratitude to Stanford R. Ovshinsky for this opportunity.

A significant contribution to the physics of the Chalcogenide Glassy Semiconductors was made by the famous model of the density of localized one-electron states, proposed by M. H. Cohen, H. Fritzsche and S. R. Ovshinsky (CFO model) [4]. During many years, the development of the physics of Chalcogenide Glassy Semiconductors (CGS) has been governed by the concepts of this model.

The following years have brought significant achievements of Stanford R. Ovshinsky as e.g. modified CGS [5] and backbone ideas about the importance of interaction between valence and lone-pair electrons [6,7]. One cannot present in an appropriate manner all the above-mentioned achievements of Stanford R. Ovshinsky in a rather brief paper like this one, and, therefore, the main aim of this communication is to discuss only the possible contribution of lone-pair electrons to the unique superconducting properties of CGS.

By now, it has been very well established that the most specific feature of chalcogenide glassy semiconductors is the presence of lone-pair electrons (LP-electrons) which belong to chalcogenide atoms and are not involved in strong covalent σ -bonding. LP-electrons create weak π -bonds, which are oriented periodically in the crystalline state and randomly in glasses. Then, according to S. R. Ovshinsky, the tail of localized one-electron states near the valence band edge is more powerful than the conduction band tail.

The LP-electrons are largely responsible for the absence of doping effect in the CGS, because they can create covalent bonds with impurity atoms, by satisfying their valence requirements. This fact, together with the flexible low-coordinated atomic structure of CGS, enables the fulfillment of famous Mott's 8-N rule for impurity atoms. Another example of the important role of the LP-electrons is the

existence of charged intrinsic defects in CGS. According to the best known scenario of R.A. Street and N.F. Mott [8] and M. Kastner, D. Adler, H. Fritzsche [9], charged intrinsic defects (or negative-U centers) mostly originate from extra covalent bonds, which consist of LP-electrons.

The purpose of the present paper is to discuss the possible role of LP-electrons in the superconductivity of CGS. First of all the previous experimental and theoretical results will be discussed, then rather new data will be presented and discussed in terms of the negative-U center model of superconductivity. The superconductivity of CGS will be compared to that of high temperature copper-oxide superconductors.

2. Experimental and theoretical results

2.1. Experimental results

The superconductivity of Chalcogenide Glassy Semiconductors has been intensively investigated by several groups of scientists [10-14], with superconductivity revealed in $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ [12], Ge_2Se_3 [13], and As_2Te_3 [11,14]. All these compounds exhibit a superconducting phase transition only under high pressure of ~ 100 kbar, with phase transition temperature T_c depending on pressure (p) and varying within several degrees. In Fig. 1, the dependences of T_c and $2E_a$ on pressure p are shown for As_2Te_3 [11,14].

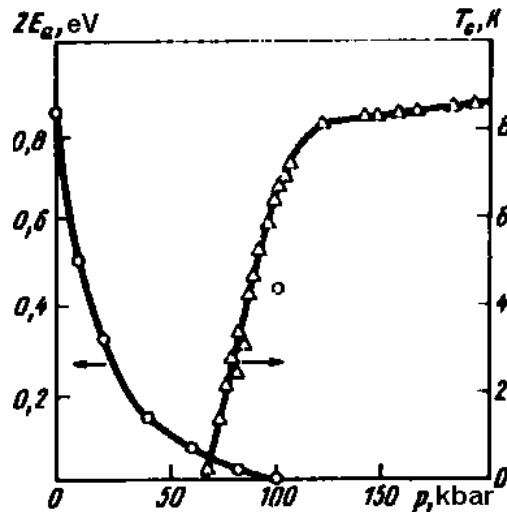


Fig. 1. Superconducting phase transition temperature T_c and $2E_a$ vs. pressure p for As_2Te_3 . E_a is the activation energy of dc conductivity: $\sigma = \sigma_0 \exp(-E_a / kT)$. Circles are data from [11], triangles are data [14]. The only circle at 100 kbar is $T_c = 4.4\text{K}$ [11].

Here E_a is the activation energy of dc conductivity: $\sigma = \sigma_0 \exp(-E_a / kT)$. The optical gap E_g is approximately equal to $2E_a$ [11], and, therefore, a conclusion is made in this paper that, up to the highest pressure, the Fermi level in the semiconducting state lies in the middle of the energy gap. The data in Fig. 1 reveal two remarkable facts.

Firstly, one can see a very strong pressure dependence of T_c . Secondly, superconductivity exists on the semiconductor side of the semiconductor – metal transition. This transition occurs at a pressure $p_g \approx 100$ kbar and corresponds to the $2E_a \approx 0$ condition. As emphasized in [14], the strong pressure dependence of T_c with $dT_c/dp \approx 0.1$ K/kbar (up to $dT_c/dp \approx 0.5$ K/kbar for Ge_2Se_3 [15]) is not observed in non-transition metals. All these features evidence that it is very difficult to apply the classic BCS theory to explain the CGS superconductivity.

2.2. Theoretical considerations

In superconductivity theories one has to ask whether the critical temperature is that at which the electron pairs (bosons) appear or that at which the gas of the already existing bosons becomes degenerate. In the classic BCS theory, pairing and Bose condensation happen simultaneously at the same temperature. This also occurs in many metallic superconductors with large conduction band width W . In these materials, the critical temperature of superconducting phase transition, T_c , is much smaller than W and approximately coincides with the energy gap Δ and pair binding energy. Contrary to this classic case, the situation when bosons exist at temperature above T_c was considered in [16,17]. After the famous paper [18], in which P.W. Anderson put forward the concept of negative-U centers, and the papers [8,9], where this idea was elaborated and the important part played by LP-electrons in the negative-U center phenomenon was emphasized, the paper [19] appeared, which was devoted to superconductivity in a system of negative-U centers. The critical temperature of the superconducting phase transition T_c is, in this case, the degeneration temperature only. Several attempts to explain the specific features of superconductivity in CGS in terms of models similar to the model described in [16,17,19] have been made. It was pointed out in [20-23] that the large dT_c/dp value can be accounted for in the framework of the bipolaronic model because of the strong dependence of the effective bipolaron mass on pressure. It is clear that this situation may arise only for large effective bipolaron mass, and this was confirmed in [24]. The dependence $T_c(p)$ was discussed for $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ in [25], and it was pointed out that mobile negative-U pairs can give rise to superconductivity at $p < p_g$. In our paper [26], we applied the results of [19] to negative-U centers in CGS and named this model the negative-U center superconductivity model (NUCS model).

2.3. Negative-U center superconductivity model (NUCS model)

In [26], the simplest chalcogenide glassy semiconductor, a-Se, was considered as an example. We use the notation of [9], and simplified structure of a-Se with two negative-U centers is presented in Fig. 2. One can see two negative-U centers: the first, C_3^+ , at the position 1 and the second, C_1^- , at the position 2 (Fig. 2a). It was assumed in [26] that, if the two centers are equivalent, they can exchange two electrons and the first center, located at the position 1, becomes C_1^- and the second, located at the position 2, becomes C_3^+ (Fig. 2b).

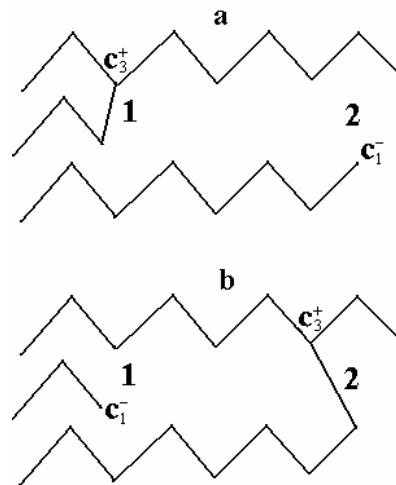


Fig. 2. Simplified structure of a-Se with two negative-U centers. Two negative-U centers can be seen, the first C_3^+ at the position 1 and the second C_1^- at the position 2 (Fig. 2a). These two centers are equivalent and can exchange two electrons, thereby changing places (Fig. 2b).

The electron exchange between C_1^- and C_3^+ may occur, e.g., through thermal activation to one-electron band states at E_c . By contrast, if the concentration of negative-U centers is sufficient, one can obtain two-electron or two-hole transport via extended states belonging to two bands. In Fig. 3, an appropriate energy diagram is shown for an isolated negative-U center and the corresponding two-electron and two-hole bands, which only appear for non-zero value of electron (or hole) site-to-site transfer integral t [27]. Here, I would like to emphasize once more that the NUCS model is based in the CGS case on the important role of LP-electrons.

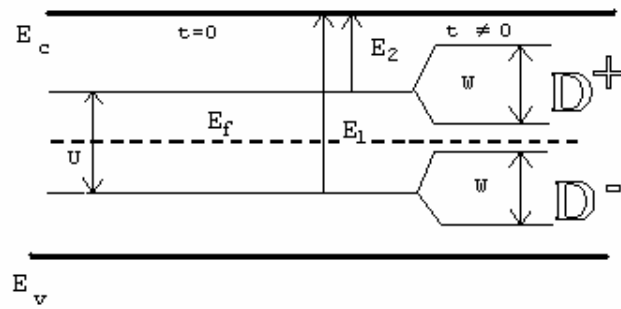


Fig. 3. The band diagram of the negative-U center model.

In [19], a simplified situation with negative-U centers of concentration N occupying sites of a simple cubic lattice with lattice constant a was considered.

We consider bosons belonging to a system of negative-U centers. The Hubbard Hamiltonian for this model is

$$H = -U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{ij\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} \quad (1)$$

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 at center i , and t_{ij} is the matrix element of transition between the nearest centers of localization (negative-U centers). It is assumed that $U > 0$ and all $t_{ij} = t \ll U$. The negative value of $-U$ leads to attraction between electrons with opposite spins at the same negative-U center. The second term in Hamiltonian (1) corresponds to the kinetic energy of band motion (width of a one-electron band $t \approx |t_{ij}|$), and the first term, to interaction (attraction) between electrons with energy U .

The classic BCS theory corresponds to the $t \gg U$ condition. We will discuss the opposite case $t \ll U$. According to the $t \ll U$ condition, the one-electron density of states consists of two narrow D^- and D^+ bands with band widths $W = 2 z t^2 / U$ [19], which are much less than the energy interval U between them (Fig. 3). The value of W is determined by transition of two electrons from one negative-U center to another. This transition is associated with virtual disintegration of a pair, then W is proportional to the effective matrix element of pair transition, t_p , between the nearest centers of localization (negative-U centers), $t_p \sim 2t^2/U$, the factor z appears owing to the use of a simple cubic lattice with $z = 6$. In Fig. 3, $E_{1,2}$ are the first and second ionization energies of an isolated negative-U center ($t = 0$). The $-U < 0$ condition is shown by the relationship between $E_{1,2}$: $E_2 - E_1 = -U < 0$. The modulus of U is the pair-binding energy needed to destroy a pair, i.e., it corresponds to Δ from the classic BCS theory, but we use U instead Δ , because it is common notation for negative-U centers.

In the case $t \neq 0$, electron pair transport at the temperature $T > T_c$ takes place along the D^- band, and hole-pair transport, along the D^+ band. When the relative concentration of electron pairs $v = n/2N$ in a set of negative-U centers lies within the interval $0 < v < 1/2$, the pair current is a result of electron pair motion in the lower D^- band. Here n is the full concentration of electrons in the set of negative-U centers. In the second case, when $1/2 < v < 1$, the pair current is due to hole pair motion in the upper D^+ band. The v value can be changed by doping with donors (acceptors), which are not shown in Fig. 3 or by altering the concentration of negative-U centers.

The composite character of bosons, which consist of two fermions (electrons for C_1^- or holes for C_3^+) residing on negative-U centers, means that a second boson cannot occupy the same negative-U center with the first boson. In other words, the strong repulsion of composite bosons at the same negative-U center exists owing to the Pauli principle for fermions. This situation leads to the following temperature T_c of Bose condensation [19]

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

The function $T_c(v)$ has a special symmetric form with maximum at $v = 1/2$, which separates the interval, where the superconductivity is due to Bose condensation of electron ($0 < v < 1/2$) and hole ($1/2 < v < 1$) bosons.

2.4. Qualitative explanation of experimental results in terms of the NUCS model

2.4.1. Chalcogenide glassy semiconductors (CGS)

Let us return to Fig. 1 and recall that the superconducting phase transition at low temperature occurs from the semiconducting state. According to [11,14], the optical gap E_g is approximately equal to $2E_a$, i.e., the Fermi level remains in the middle of the optical gap at any pressure. Then one can suggest that it is very difficult to apply the classic BCS theory of superconductivity to this case, because, according to this theory, the Fermi level must lie in the conduction band. By contrast, the semiconductor-superconductivity phase transition has a very simple and natural explanation in terms of the NUCS model. Indeed, let us suppose that pressure makes the distance "a" between negative-U centers shorter and the transfer integral t larger. Then, at the critical pressure p_c , bands D^+ and D^- may be formed and Bose condensation of bosons in these bands gives a superconducting phase transition at T_c . Here, I would like to emphasize once more, that the conductivity experimentally observed at high temperature $T > T_c$ is due to one-electron band states with rather small effective mass $m^* \sim m_0$, which are situated near E_c or E_v . The transport of electron or hole pairs makes a very small contribution to the conductivity experimentally observed at high temperature $T > T_c$, because pairs have large effective mass $m^* \sim 25m_0$ [24]. And only the superconductivity current observed in the temperature interval $T < T_c$ takes place in the two-electron or two-hole bands (D^+ and D^-). Thus, in the NUCS model, the current at $T > T_c$ and the superconductivity current at $T < T_c$ are due to different groups of carriers. The strong pressure dependence of the transfer integral t well accounts for the large value of dT_c/dp , as pointed out in [21,24]. One can see from Fig. 1 that the dT_c/dp value becomes small when the real semiconductor-metal transition ($2E_a = 0$) occurs.

The NUCS model was applied in [26] to channels formed in switching in a thin CGS layer. Typical radius of the channel or current filament, R , is ~ 1 micron. It was assumed that a large concentration of negative-U centers appears reversibly in these channels. D^+ (or C_3^+ according to [9]) centers appear owing to the response of the active region of the channel to the pressure arising during the switching event. The large number of C_3^+ centers with $z = 3$, which exceeds $z_0 = 2$ for chalcogenide atoms, relieve the stress inside the channel. Commonly, the concentration D of negative-U centers in CGS is 10^{16} - 10^{18} cm $^{-3}$. We have to assume that D increases up to 10^{19} - 5×10^{19} cm $^{-3}$ in order to account for by formulas (2) the temperature on the order of 300 K and higher.

2.5. Mixture of chalcogenide glassy semiconductors with high temperature oxide superconductor (HTSC)

In [28,29], very interesting experimental results concerning the superconductivity in a-Se - $Y_1Ba_2Cu_3O_7$ were presented. A mixture of glassy Se with microcrystalline pieces of an HTSC compound, $Y_1Ba_2Cu_3O_7$, with $T_c \approx 90$ K were investigated in these papers. Microcrystalline pieces of $Y_1Ba_2Cu_3O_7$, having linear dimensions of about several micrometers, occupy approximately 14% of the whole volume, and, therefore, all of them are separated by a-Se, as shown in Fig. 4 from [28,29]. At

high temperature $T > T_c$, the conductivity of samples was on the order of $10^{-6} \Omega^{-1} \text{ cm}^{-1}$. This value strongly differs from the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ conductivity of $\sim 10^3 \Omega^{-1} \text{ cm}^{-1}$ and shows that at high temperature the conductivity is governed by doped a-Se. It is known that pure a-Se has a conductivity on order of $10^{-12} \Omega^{-1} \text{ cm}^{-1}$, which may be increased by many orders of magnitude through doping with oxygen.

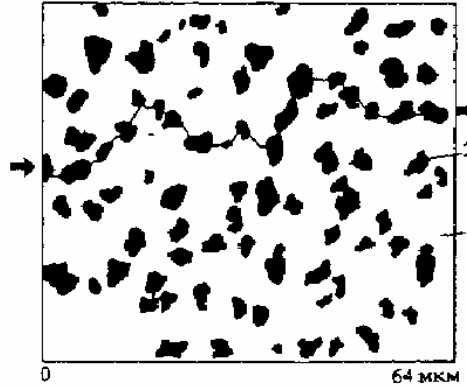


Fig. 4. Mixture of glassy Se (white region-1) with microcrystalline pieces of HTSC compound $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ (black regions-2). The superconducting infinite cluster is represented by a solid black line shown as guide for eye.

The transition temperature T_c of the mixture was the same as for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$, i.e., $T_c \approx 90 \text{ K}$ and the superconductivity current existed at this temperature throughout the sample. However, the mean distance between microcrystalline pieces of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ was very large. It was equal to several micrometers, i.e., exceeded by more than a factor of 10^3 the correlation length ξ equal to $10\text{-}15 \text{ \AA}$ in $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$. In [28,29], we assumed that microcrystals of HTSC are connected by channels which are similar to those appearing in switching in CGS. A large number of negative-U centers may exist in the channel owing to self-compensation induced by doping with oxygen. Additional concentration of negative-U centers may be generated during the switching in the internal electric field or in the weak external electric field used in measurements. The superconductivity in the system of negative-U centers in the channel may be induced by superconducting phase transition in microcrystalline pieces of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$, which occupy two ends of each channel.

2.6. High temperature oxide superconductors

In [27], we demonstrated that the NUCS model can account for several important experimental facts concerning high temperature oxide superconductors. It was shown, firstly, that formulas (2) can explain the high value of T_c . The tunneling integral t between the nearest copper cations is $\sim 50 \text{ meV}$ [30]. If one takes $t=50 \text{ meV}$, $U=1.8 \text{ eV}$, $\nu=1/2$, and $z=6$, then the experimentally observed high value of $T_c \approx 90 \text{ K}$ for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ may be obtained from (2). Thus the NUCS model can explain the high value of T_c on the basis of the experimentally determined parameters and U modulus equal to 1.8 eV . It should be noted here that the inequality $t \ll U$ is very well satisfied.

The second fact we would like to underline is the following. It is known that many high- T_c metal oxides demonstrate a special nonmonotonic (with a maximum) dependence of T_c on composition [31-39]. There have been several attempts to explain this dependencies by the special form of the Fermi surface in terms of the BCS theory. The present NUCS model explains the nonmonotonic dependence of T_c on composition very naturally as a change from superconductivity due to electron pair transport ($\nu < 1/2$) in the D^- band to superconductivity governed by the hole pair transport ($\nu > 1/2$) in the D^+ band. Then the maximum in the curve corresponds to $\nu = 1/2$. For example, the relevant results for the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$ system are presented in Fig. 5 from [27].

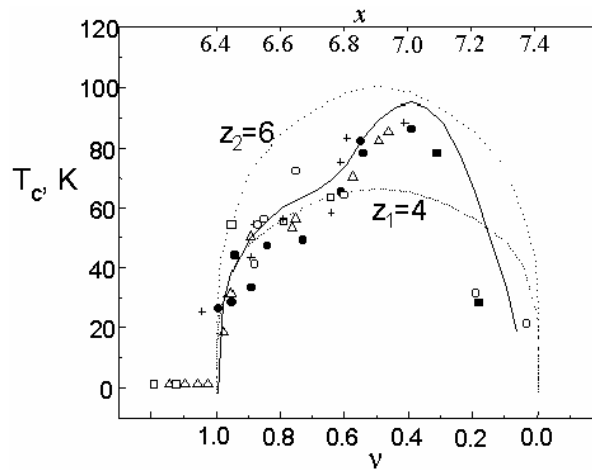


Fig. 5. Theoretical (dotted and dashed lines) and experimental T_c dependencies for $Y_1Ba_2Cu_3O_x$ system [27]. A solid black line shown as guide for eye for experimental data.

The x and ν values are related by: $\nu = 7.4 - x$ [27]. Theoretical results corresponding to formulas (2) are depicted by dashed ($z_1=4$) and dotted ($z_2=6$) lines. The change from $z_1=4$ to $z_2=6$ is necessary in order to take into consideration the structural phase transition at $x = 6.7$.

I would like to emphasize once more that the most important feature of Fig. 5 is the coincidence of the non-monotonic (with a maximum) experimental and theoretical $T_c(\nu)$ dependencies.

In terms of the NUCS model, charge carriers in normal and superconducting phases may be different. In the normal phase, carriers in $Y_1Ba_2Cu_3O_x$ are holes from the valence band, because they have relatively small effective mass. The superconducting current is due to coherent movement of pairs along D^+ (or D^-) bands.

This fact allows us to explain the superconductivity, which arises from the semiconducting state, as seen in Fig. 6 for $x < 6.5$ [40].

From the standpoint of the NUCS model, this means that the Fermi level in the nonsuperconducting (semiconducting) state lies between the D^+ and D^- bands and the current at $T > T_c$ takes place owing to one-electron states at the valence band edge E_v . The superconducting phase transition occurs through Bose condensation in the D^+ band, because $\nu = 7.4 - x > 0.9$ at $x < 6.5$.

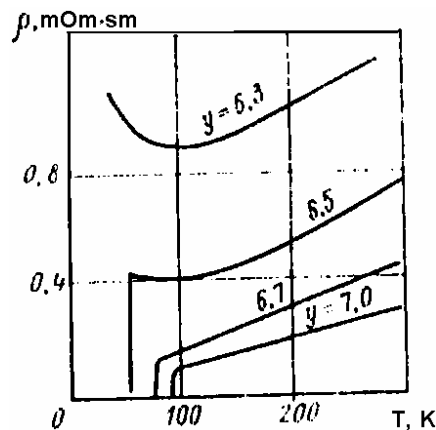


Fig. 6. Temperature dependencies of resistivity for $Y_1Ba_2Cu_3O_y$ [40].

2.7. Comparison of CGS and HTSC data

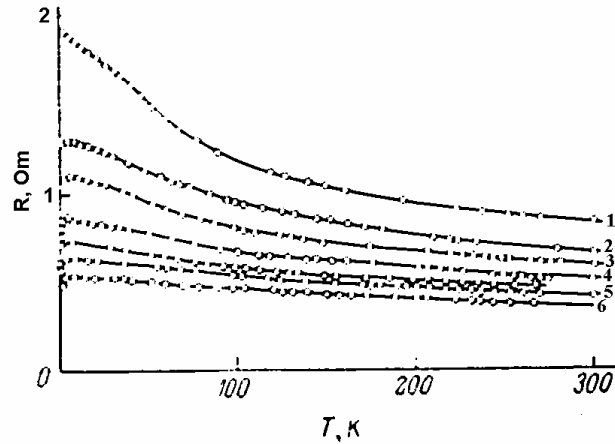


Fig. 7. Temperature dependencies of Ge_2Se_3 resistance at different pressures p [13]. p , kbar: 190 (1), 200 (2), 210 (3), 220 (4), 230 (5), 235 (6).

Similar dependencies have been observed for $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ [12] and As_2Te_3 [14]. It is worth noting that all these curves are very similar to those from Fig. 6 for HTSC materials. In both cases, the superconductivity originates from the semiconducting state. From the standpoint of the NUCS model, the pressure raises in the CGS case the concentration of negative-U centers and induced D^+ and D^- bands by decreasing the distance "a" between negative-U centers. In the HTSC case, a similar decrease in "a" is due to an increase in the concentration of negative-U centers in samples, which are doped with oxygen to a greater extent.

The crucial parameter in the NUCS model is the transfer integral t proportional to $\exp(-2a/r_0)$, where r_0 is the radius of a one-electron wave function of a negative-U center. From formulas (2) one can see a very strong dependence of T_c on $t \sim \exp(-2a/r_0)$. In [41], it was shown theoretically that replacing oxygen with chalcogens, namely, sulfur and selenium, may raise T_c through an increase in t (or r_0). This was done in [42], and a slight increase in T_c was observed. However, the authors of [42] could not prepare samples with large amount of S and Se by synthesis. Phase separation occurred and they obtained an inhomogeneous mixture.

Here I would like to recall an excellent paper [5] by Stanford R. Ovshinsky, in which he put forward, together with co-authors, the concept of a modification technique, preventing phase separation in the case of a significant amount of dopants. I hope that this technique may be useful for preparing homogeneous, maybe non-crystalline HTSC films, with significant amount of S and Se and increased T_c .

3. Conclusions

The importance of LP-electrons in numerous physical phenomena in the CGS is well known. They play a crucial role in the appearance of negative-U centers in these materials. The negative effective correlation energy is due to energy gain, which is mostly the LP-bond energy. Thus, in the ground state, there is strong attractive interaction of two electrons (holes), which exceeds Coulomb repulsion, i.e., the reaction



becomes exothermic. The NUCS model employs the existence of a considerable amount of negative-U centers to form pair-carrier band states. Bose condensation of pairs (bosons) gives rise to superconductivity. I suggest that many specific features of superconductivity in chalcogenide glasses

are due to superconductivity of a system of negative-U centers, rather than to the BCS nature of the phenomenon.

As to metal oxides, it is known that the disproportionation reaction occurs in these materials. For example, the disproportionation reaction occurs in $Y_1Ba_2Cu_3O_x$ as follows:



This reaction, which parallels that of (3), suggests that the NUCS model is applicable to cuprates. Here, I would like to emphasize the following. Cu^{n+} denote structural units consisting of a copper ion and its oxygen environment. At present, no appropriate data are available that could be used to construct quantitatively these units, as it has been done for chalcogenide glassy semiconductors. However, we assume that different charge states Cu^{n+} correspond to different positions of oxygen ions in the Cu-O-Cu chain and it may be suggested that LP-electrons of oxygen account for the exothermic nature of reaction (4).

Acknowledgements

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