

THE THERMOPOWER IN THE TEMPERATURE RANGE T_c -1000K AND THE BAND SPECTRUM OF BI-BASED SUPERCONDUCTORS.

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The temperature dependencies of thermopower, S , in the range $T=T_c$ -1000K as well as of resistivity and Hall coefficient in the range $T=T_c$ -300K for the single-phase ceramic samples $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Nd}_x\text{Cu}_2\text{O}_y$ have been measured. It was found that the $S(T)$ dependencies in normal phase have three characteristic regions. Despite the fact that the $S(T)$ dependencies in Bi-based high- T_c superconductors (HTSC) differ essentially from ones in Y-based HTSC at $T=T_c$ -300K, the main feature of theirs ($S(T)=\text{const}$ at high temperatures) retains in samples investigated at $T>620\text{K}$. The results obtained have been analyzed on the basis of the narrow-band model with the use of assumption of slight asymmetry of the conductive band. The band spectrum parameters of the samples studied have been calculated. An analysis of the tendencies in these parameters changes with samples composition varying enables to make the conclusion about the similarity of the main features of the conductive band structure in Y- and Bi-based HTSC.

1. INTRODUCTION

It is hard to tell now something definitely about the band structure in Fermi level vicinity of the Bi-based HTSC. The complex experimental investigation of the transport phenomena is one of the most available method for the band spectrum study and is reasonably effective one at the same time. This is confirmed convincingly by the experience on the investigations of semiconductors and semimetals with a complicated electron spectrum. The information extracted from such an investigation becomes more detailed and unambiguous if we can vary the Fermi level position over a wide range of energy. This is usually achieved by doping material studied with donor or acceptor impurities.

Earlier we have proposed the phenomenological model of electron transport in the case of narrow conductive band [1]. This so-called narrow band model has enabled us not only to explain all the specific features of transport coefficients temperature dependencies, but also to determine the band spectrum parameters in the samples with different composition. On the basis of analysis of tendencies in these parameters change we have made some conclusions about conductive band transformation character, influence of different components of unit cell and have revealed the correlation between band spectrum parameters and critical temperature (T_c) value in the Y-based HTSC [1-3]. To realize this approach, as applied to the Bi-system, we have chosen the 2212-phase as a main object of the investigation. Compared to the 2223-phase this one is more stable that enables us to prepare highly doped samples being single-phase.

It is known that temperature dependencies of resistivity (ρ) and Hall coefficient (R) in Bi-system are like the ones in Y-system (see, for example, [4]). However the $S(T)$ dependencies differ essentially from the ones in Y-based HTSC [5,6]. It generates a need for some additions to our model for explaining these dependencies. On the other hand data about Seebeck coefficient behavior at $T>300\text{K}$ are practically absent in the literature although they can be quite informative in the view of band spectrum studying.

In this connection in this paper we carried out the experimental investigation of thermopower in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Nd}_x\text{Cu}_2\text{O}_y$ ($x=0-0.5$) in the wide temperature range as well as analysis of the narrow band model applicability to Bi-based HTSC.

2. RESULTS AND DISCUSSION

The ceramic samples $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Nd}_x\text{Cu}_2\text{O}_y$ have been prepared by standard solid-state synthesis method from high-purity oxides and carbonates. The absence of heterogeneous phases in the appreciable amount was controlled by using the X-ray analysis as well as by comparative analysis of magnetic susceptibility and transport coefficients temperature dependencies.

Table 1

The values of transport coefficients in normal phase and critical temperature in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Nd}_x\text{Cu}_2\text{O}_y$

x	$\rho(300\text{K})$, $\text{m}\Omega\text{-cm}$	$\rho(100\text{K})$, $\text{m}\Omega\text{-cm}$	$S(300\text{K})$, $\mu\text{V/K}$	$R(300\text{K})$, $\times 10^{-3}\text{cm}^3/\text{C}$	T_c^m, K	T_c^o, K
0.0	1.2	0.6	-3.70	1.9	76.6	64.2
0.1	2.7	1.4	-2.08	2.9	83.9	66.0
0.2	3.0	2.0	2.17	4.2	82.6	56.9
0.3	3.5	2.9	6.30	6.8	75.9	53.9
0.4	3.8	3.7	15.82	9.6	56.0	34.2
0.5	11.1	9.4	31.10	12.5	36.0	23.5

The results of electro-physical measurements are shown in Table 1. The Nd content increase leads to increasing of the absolute values of ρ , S , and R as well as T_c depression and broadening of superconducting transition. The temperature dependencies of ρ and R are similar to the typical ones for all the HTSC materials. Dependencies of $\rho(T)$ are linear in all the temperature range measured, the Hall coefficient decreases with the temperature increase, although the relative lowering of R for Bi-system is not so great as for Y-system. The $S(T)$ dependencies are shown in Fig.1. These curves are stationary, i.e., they don't change after several temperature cyclings. It can be seen from this figure that the absolute value of S increases with x and the $S(T)$ dependencies in normal phase have three characteristic regions. At $T=T_c-(120-200)\text{K}$ the thermopower have the smooth maximum which is characteristic also to Y-system. At $T=(120-200)\text{K}-620\text{K}$ one decreases almost

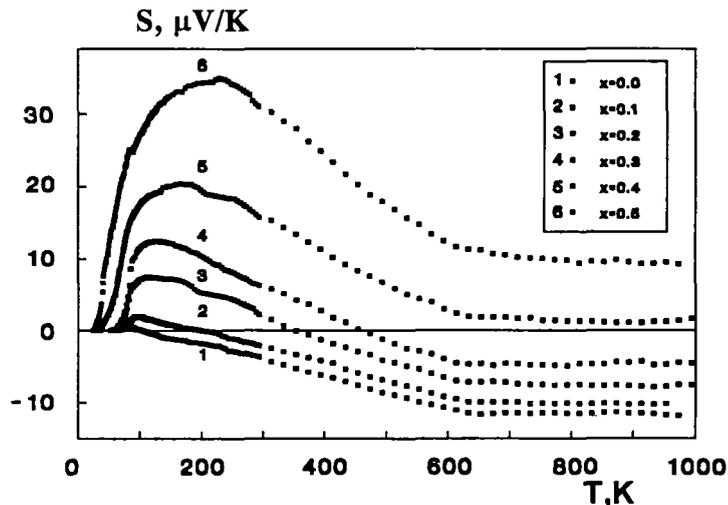


Fig.1. The temperature dependencies of thermopower in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Nd}_x\text{Cu}_2\text{O}_y$

linearly which is characteristic to Bi-based HTSC as compared with Y-based ones. Nevertheless the main feature of $S(T)$ dependencies in Y-based HTSC ($S(T)=\text{const}$ at high temperatures) retains in Bi-based HTSC at $T>620\text{K}$. The great length of S linear decrease region (300K) and very insignificant deviation from $S=\text{const}$ at high temperature have engaged our attention. The last fact is forcible argument in favor of the narrow band model using because its main consequence is just independence of S in the limit of high

temperature. Furthermore, yet another fact can be noted. This is the quite drastic transition from second region of $S(T)$ dependencies to third one with independence of the temperature of this transition ($T=620K$) from dopant content. It is necessary to emphasize that analogous point of drastic transition from one dependence type to another was been detected by us in Y-based HTSC [7], although at another temperature ($T=350K$). It is possible that existing of this point is a common feature of different types of HTSC.

For explanation and quantitative describing all the experimental data obtained we must bear in view the concrete model of band spectrum with the lowest number of fitting parameters. For this purpose we are using (as in the case of Y-based HTSC) the narrow-band model which suggests the band width to be comparable with the Fermi smearing. The analysis of the main electron transport peculiarities in case of narrow band is performed in Ref.[1]. Certain of the concepts and results of this analysis are as follows.

The model includes three phenomenological parameters. The first one is the degree of band filling with electrons that is the ratio of the free electrons number to the whole number of band states. Two other parameters are the "state density" and "conductivity" effective band widths (W_D and W_σ). These effective widths may differ from one another as well as from the whole band width W . The distinctions between W , W_D , W_σ are related to the peculiarities and differences in energy dependencies of electron state density $D(E)$ and differential conductivity $\sigma(E)$. The comparison of W_D and W_σ values may be used to get some information on the electron kinetics, dynamics and scattering peculiarities. As shown in Ref.[1], in the case of narrow band (i.e., when the W value is not much greater than k_0T value) the spectrum details, like the $D(E)$ and $\sigma(E)$ peculiarities, are not of great significance as long as the W_D and W_σ values. This makes possible to use the simplest approximations for these functions as rectangles with different widths. In this case we can derive the analytical expressions for chemical potential and all the transport coefficients. It is to be noted that our formulas enabled us to compute the absolute value and the sign of the Seebeck coefficient at the different temperatures, whereas the ρ and R could be computed only with an accuracy of a constant cofactor. Therefore we have used $S(T)$ dependencies to determine the model parameters values and then we have verified their validity by comparison between the calculated and experimental dependencies of the $\rho(T)/\rho(300K)$ and $R(T)/R(300K)$. In the limit of high temperature (when $W_D < k_0T$) Seebeck coefficient doesn't depend on temperature and is determined from formula:

$$S = \frac{k_0}{e} \cdot \ln \frac{F}{1-F}$$

It should be mentioned that the fitting parameters are believed to be temperature-independent. That means that the parameters number is less than the number of equations which we can use for their determination because we compare the calculated and experimental temperature dependencies in a wide temperature range.

When analyzed the transport coefficients in Y-based HTSC we have proposed that the conductive band is symmetric. For explanation of $S(T)$ dependencies in Bi-based HTSC we use narrow band model too but we add assumption of slight asymmetry of the conductive band. This fact is taken into account by introducing some distance ($b \cdot W_D$, where b is asymmetry parameter) between centers of rectangles $D(E)$ and $\sigma(E)$. In this case all the formulas from Ref.[1] retain their previous form but in formulas for transport coefficients instead of the chemical potential μ we must use now $(\mu - b \cdot W_D)$.

In the framework of our model we were able to describe the temperature dependencies of thermopower in the whole temperature range adequately. The region of drastic transition $S(T)$ from linear decrease to constant value is of particular complexity. The calculated dependencies demonstrate only smooth transition which may be due to roughness of approximation used. It is necessary to take into account the features of the band structure in more detail for the best agreement of experimental and calculated dependencies. In particular it would appear reasonable that the band spectrum parameters are temperature dependent. Nevertheless, analyzing the results obtained we can consider with reasonable

confidence that our data lend support to the validity of narrow band using for Bi-based HTSC. It is necessary to emphasize that calculated dependencies of $\rho(T)$ and $R(T)$ retain all its features in the frame of asymmetric model.

The dependencies of the main band parameters calculated from $S(T)$ on Nd content are shown in Fig.2. It can be seen that the deviation from stoichiometry (increase of x in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Nd}_x\text{Cu}_2\text{O}_y$) leads to increase of F value (the hole density decrease) as well as to the appreciable transformation of conductive band. The effective band width gradually increases with x , in so doing this broadening of band is accompanied by simultaneous reduction of W_σ/W_D ratio as shown by our calculations. Therefore, we could assume that

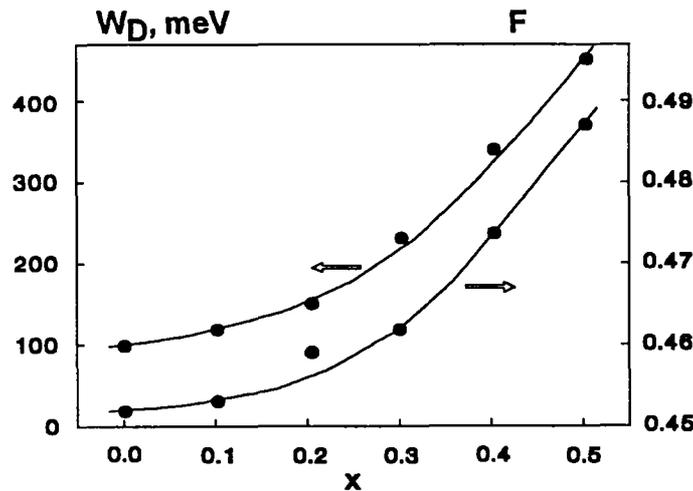


Fig.2. The band effective width and the band filling degree with electrons vs. Ca content.

increase of dopant content leads to the growth of the difference between the energy dependencies of $D(E)$ and $\sigma(E)$ functions and as consequence the W_σ/W_D ratio changes. One of possible explanation of the band transformation revealed bases on assumption of determinant effect of lattice disordering. The rise of disorder causes the Anderson's localization of states at the band edges and increasing of total band width. Thus, the values and the changes character of band structure parameters with deviation from stoichiometry, as well as the possible reason of these changes in Y- and Bi-based HTSC are analogous. As for the band asymmetry, our calculations show this one to be very little (the energy shift of $D(E)$ and $\sigma(E)$ rectangles relative to each other is about 3-5% from the total effective band width).

The results obtained enable us to reveal (as in the case of Y-based HTSC) a correlation between the band spectrum parameters and the critical temperature value. With the proviso that the number of states in the band remains constant, the band broadening causes the decrease of the density of states value at Fermi level. It may be one of the factor (perhaps, the main factor) leading to suppression of the T_c value with deviation from stoichiometry.

3. CONCLUSION

In summary, we have carried out the investigation of thermopower behavior in ceramic samples $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Nd}_x\text{Cu}_2\text{O}_y$ in the wide temperature range. The results obtained and their analysis allow to make the following conclusions.

1. There are two lengthy regions in the $S(T)$ curves for Bi-2212 HTSC with different character of S behavior. The thermopower value decreases linearly with temperature up to $T=620\text{K}$ and remains constant above this temperature.
2. The transition from one type of dependence to another is very drastic. As this takes place, the temperature of this transition ($T=620\text{K}$) is unchanged for the samples with different degree of the deviation from stoichiometric composition.

3. The narrow band model can be used successfully for explanation of the unusual behavior of the transport coefficients not only in Y-system, but also in 2212-phase of Bi-based HTSC. Some literature data provide reason to believe that band narrowness is the common feature of all known high- T_c materials.

4. The values and the changes character of band structure parameters with deviation from stoichiometry as well as the correlation between these parameters and critical temperature in Bi-based HTSC are analogous to the ones in the Y-system. This clearly demonstrates the similarity of main properties of charge carriers system in these types of HTSC-materials.

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