SUPERCONDUCTING PROPERTIES OF SINGLE CRYSTAL WIRES OF LEAD TELLURIDE DOPED WITH THALLIUM

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Abstract

Results of the measurements of temperature dependences of resistivity of thin single crystal wires of PbTe<Tl> in the temperature region 0.4 ÷ 4.2 K are presented. Thallium average concentration was 0.001 ÷ 0.02 at.%. Single crystal wires (with diameters d = 5 ÷ 100 μm) were obtained by filling of quartz capillary with the solution melt with the following directed crystallization of this material. The structural perfection of investigated samples was tested by X-ray diffraction and LAMMA analysis. It is revealed, that at low temperatures in single crystal wires of PbTe<Tl> transition in a superconducting state is observed. The temperature of transition correlates with impurity concentration (for single crystal wires of PbTe<Tl> at thallium concentration 2% T_c=2,1K).

Mechanisms leading to superconducting transition and features of temperature dependence of resistance in the field of previous transition are discussed. The interpretation of the obtained results is given based on model of an impurity with skipped valence.

1. Introduction

The narrow-gap semiconductors of type A_4B_6 themselves are unique objects both from the point of view of theoretical investigation and in applied aspect. For all this many new unique properties are shown and associated with doping of the given materials with various impurities. Doping of semiconductor compounds of type A_4B_6 with elements of III group leads to a number of features in their electro physical and optical properties [1-2]. This explains the interest to such materials and, in particular, to semiconductor compound PbTe<Tl> as to the most striking example in which a lot of unique properties have been observed. Dramatic influence of Tl content on superconducting properties is the main feature of PbTe<Tl> semiconductor [3]. Specific action of thallium consists in the following: thallium impurity generates in the range of the permitted band states of a valence band an impurity band that leads to essential change of density of band states. It leads to essential change of transport coefficients, which are determined by density of states, by the form of the impurity band and by the relative position of the Fermi level [1, 2]. On the other hand, thallium is an impurity element of III group in the compounds A_4B_6, which shows a skipped valence [4]. It means that thallium can have the valence from 1 up to 3, and the most unstable is the state with a bivalent impurity – thallium atoms have one s-electron on the external shell. In such case they should dissociate as [5]: $2Tl^{2+} \rightarrow Tl^{1+} + Tl^{3+}$, because states with valence 1 and 3 are more suitable from the viewpoint of energy. Theoretical description of this assumes existence of the centers with negative correlation energy U: $U_n = (E_{n+1} - E_n) - (E_n - E_{n-1}) < 0$, where valence number n takes the values 1, 2, 3.

Theoretically it has been predicted, that the presence of the U-centers can lead to those features in electro physical properties which were observed in the system PbTe<Tl> [5]. Such a behavior of an impurity of thallium in PbTe is similar to Kondo effect in metals and should be shown in particular on the superconducting properties of this compound [6]. From this point of view in the present work an attempt of interpretation of experimental data of the research of superconducting properties of PbTe<Tl> single crystal wires is undertaken.

2. Experimental results and discussion

Single crystal microwires of PbTe<Tl> (diameter d = 5 ÷ 100 μm, length l ~ 20 cm) with thallium average concentration N_{Tl} = 0.001 ÷ 0.02 were grown in the following way [7]. Initial material of corresponding chemical composition was placed into a quartz tube (diameter – 15 mm). The bulk material was prepared in the following way. Since pure Tl oxidizes in the air quickly and greatly, it is necessary for a preparation of initial mixtures to use compounds of thallium - in our case TlTe. Syntheses of polycrystalline materials $(PbTe)_{1-x}(TlTe)_x$ of corresponding compounds were made in the quartz tube in the hydrogen atmosphere. Over the material a bunch of quartz capillaries is situated. The choice of quartz as the material for capillaries is limited by high temperature of its softening, what must be higher than the melting temperature of the material. The tube was evacuated up to residual pressure $10^{-2} \div 10^{-3}$ Pa and placed in vertical zone furnace, in which the temperature on the whole length of the capillary is the same and higher than the melting temperature of the material ($T_{melt} < T < T_{soft}$). After melting of the material the capillary with open lower ends was put down in the melted material to a depth of 5÷10 mm. Afterwards in the tube pressure rose (inert gas (argon) pressure of $10^5 \div 10^6$ Pa was used) under which capillary was filled with the melting liquid material. Crystallization of the melted material was realized directly beginning from soldered ends to the open ones at the expense of move of the furnace (rate of the move may be changed and makes up several centimeters per hour). Construction of apparatus ensures conditions under which growth of the microwires is nucleated at the closed ends of the capillaries, this allowing surplus liquid material to flow out and avoiding of mechanical tensions. The given method of obtaining of single crystal microwires allows producing samples with different diameters under the same growth conditions with high structural perfection. The structural quality was tested by X-ray diffraction and Laser Microprobe Mass Analyzer (LAMMA).

The samples for the measurements were prepared in the following mode. A sample of the corresponding diameter was chosen from the set of crystals. As the initial sample has glass isolation, it was preliminary subjected to selective etching in a solution of acid HF. Reliable electrical contact was made using eutectic In-Ga. Measurements have been executed both on samples with different diameters and on samples of equal diameters. Temperature measurements were carried out by means of thermocouple Cu – (Cu + 0,04 at % Fe), by means of platinum resistance thermometer or the graduated resistance temperature detector. Such thermocouple makes it possible to carry out experiments with high precision in low temperature region.

In Fig.1 temperature dependences of resistivity vs temperature of single crystal microwires of PbTe<Tl> are shown. The analysis of temperature dependences of resistivity shows, that in the doped samples the superconducting behaviour with T_c > 0.4 K appears at x > 0.01. Specimens with lower thallium concentration starting with T = 30÷40 K exhibited negative temperature coefficients of resistance down to T = 0.4 K. Typical temperature dependences of resistance are presented in Fig. 1, 2. One can see that in wires with d < 50 μm superconducting transition is many-step and incomplete. This result is in agreement with the one of resistive measurements [8], obtained in assumption of availability regions with different concentrations of impurity.

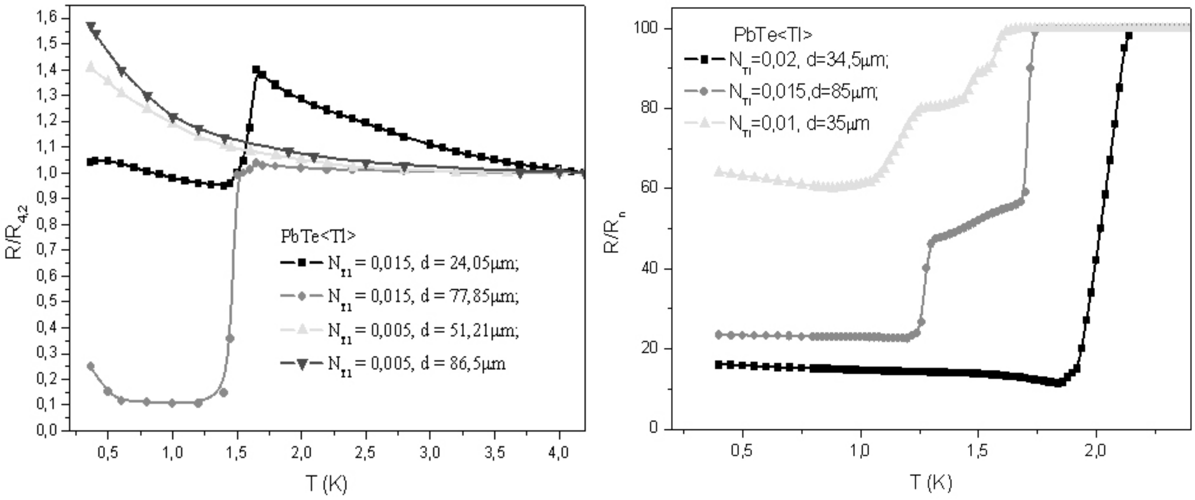

Fig.1. Temperature dependences of resistivity in the region of low temperature of singlecrystal wires of PbTe<Tl>.

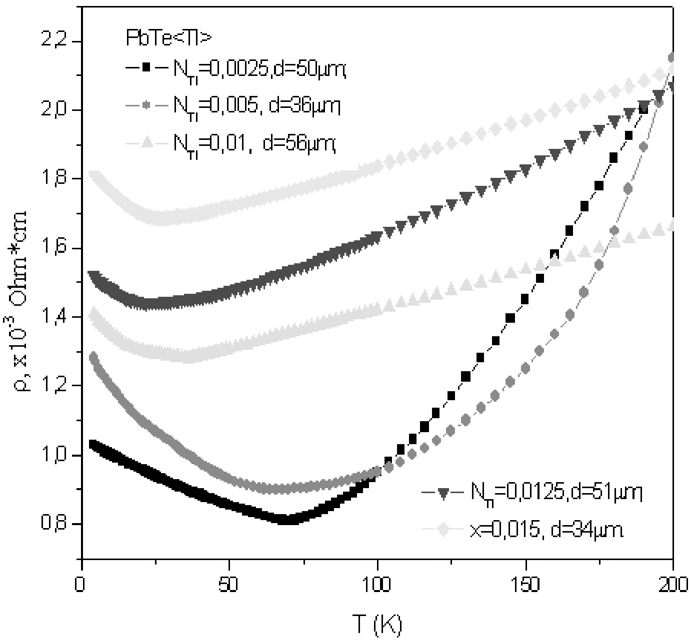

Fig.2. Temperature dependences of resistivity of single crystal wires of PbTe<Tl>.

From the moment of discovery of superconductivity in system PbTe <Tl> traditionally the mechanism for explanation of the superconductivity was based on the supposition that the resonant states of an impurity play a decisive role [1, 2].

It is necessary to note however that the greatest part of results on research of properties of these materials has been obtained on the samples prepared by pressing from powder. The results obtained on single crystal samples showed a lot of unusual properties, which did not find an explanation basing only on the presence of an impurity band of resonant states [9, 10]:

- starting with T = 30÷40 K samples exhibited negative temperature coefficients of resistance down to T = 0.4 K;
- all samples demonstrated negative magnetoresistance at helium temperature.

The analysis of temperature dependences of resistivity of single crystal wires of PbTe<Tl> in the whole range of concentration of a doping impurity at low temperatures shows that the appearance of the resistance minimum is characteristic. It is known [11] that in systems with magnetic impurity the appearance of low temperature minimum of resistivity is provided by the interaction of the carriers with the magnetic moments of impurities. For all that the essential moment is the fact, that quantum fluctuations of valence according to theoretical calculations can stimulate formation of the Cooper pairs and finally result in superconducting state in the given materials [12].

3. Conclusions

In the present work the results on research of resistive properties of single crystal wires of PbTe<Tl> (N_{Tl}=0.001 ÷ 0.02, d = 5 ÷ 100 μm) in a wide range of temperatures are presented. The principal task of research was the analysis of the experimentally established features of resistive properties of these systems in the range of low temperatures. For all investigated samples at low temperatures anomalies in the temperature dependence of resistance are observed. Considering features of behavior of thallium impurity in lead telluride and comparing the obtained results with similar for metals with magnetic impurity it is possible to conclude that the reason of the observed anomalies is charge Kondo effect associated with skipped valence of Tl impurity states shown in PbTe.

References

[1] V.I. Kaidanov, Y.I. Ravich, Sov. Phys. Usp, 145, 51, 1985.
[2] S.A. Nemov, Y.I. Ravich, Sov. Phys. Usp, 168, 817, 1998.
[3] I.A. Chernik, S.N. Lykov, Sov. Fiz. Solid State, 23, 1400, 1981.
[4] B.A. Volkov, L.I. Ryabova, D.R. Khokhlov, Sov. Phys. Usp, 172, 875, 2002.
[5] I.A. Drabkin, B.Y. Moizhes, Sov. Phys. Semicond. 15, 357, 1981.
[6] Y. Matsushita, H. Bluhm, T.H. Geballe, I.R. Fisher, Phys. Rev. Lett., 94, 157002, 2005.
[7] N.I. Leporda, A.D. Grozav, Moldavian Journal of the Physical Sciences, 1, 74, 2002.
[8] M.P. Boiko, D.V. Gitsu, E.A. Zasavitsky, A.S. Sidorenko, Sov. Phys. Semicond., 21, 1303, 1987.
[9] K.I. Andronik, V.F. Banar, V.G. Kantser, A.S. Sidorenko, Phys. Stat. Sol. (b), 133, K61, 1986.
[10] A.S. Sidorenko, E.A. Zasavitsky, Sov. Phys. Semicond., 20, 2120, 1986.
[11] A.A. Abrikosov, Bases of the theory of metals, Nauka, Moskow, p.91., 1987.
[12] M. Dzero, J. Schmalian, Phys. Rev. Lett., 94, 157003, 2005.