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# Low-temperature anomalies of the hardened tin conductivity

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The low-temperature anomalies of conductivity of tin's filaments obtained by cooling of the melt from $T$ ~ (800–900) K with velocity $v$ ~ $10^2$ K/sec are investigated. The samples showed signs of hardening demonstrate the electro-physical and structure abnormalities at the helium temperatures in comparison with superconducting β-Sn modification. Arguments are presented that the semiconducting phases are supercooled allotropic modifications γ- and $x$-Sn which exist in equilibrium states above $T$ ~ 430 K.
**Keywords:** low-temperature conductivity, tin's filaments, structure abnormalities

Исследованы низкотемпературные аномалии проводимости оловянных нитей, полученных в результате охлаждения расплава от $T$ ~ 800–900 К со скоростью $v$ ~ $10^2$ К/с. Образцы с признаками закалки демонстрируют при гелиевых температурах электрофизические и структурные аномалии по сравнению со сверхпроводящей модификацией β-Sn. Приведены аргументы относительно того, что полупроводниковые фазы представляют собой переохлажденные метастабильные аллотропические модификации γ- и $x$-Sn, существующие в равновесном виде выше $T$ ~ 430 К.

**Низькотемпературні аномалії провідності загартованого олова**. *В.М.Воєводін, В.І.Соколенко, В.О.Фролов*.

Досліджено низькотемпературні аномалії провідності олов'яних ниток, добутих в результаті охолодження розплаву від $T$ ~ 800–900 К зі швидкістю $v$ ~ $10^2$ К/с. Зразки з прикметами загартування демонструють при геліевих температурах аномальні електрофізичні і структурні властивості у порівнянні з надпровідниковою модифікацією β-Sn. Наведено аргументи відносно того, що напівпровідниковими фазами є переохолоджені метастабільні алотропічні модифікації γ- і $x$-Sn, існуючі у рівноважному вигляді вище $T$ ~ 430 К.

## *1. Introduction*

It was considered until recently [1] that tin (Sn) at atmospheric pressure may be found in one of three equilibrium allotropic modifications — α-, β- and γ-Sn separated by transformation's temperatures ($T$) $T_{\alpha\text{-}\beta}$ ~ 286 K and $T_{\beta\text{-}\gamma}$ ~ 430 K. The temperature dependences of electrical resistance ($R$) and thermo EMF ($S$) of high-purity Sn single crystals has been demonstrated in [2] and for the first time it has been reported an existence of the fourth Sn allotropic modification of higher thfn ~(470–480) K, which the authors called $x$-Sn, Fig. 1.

It is known that α-Sn (gray tin) is not a superconductor, while β-Sn (white tin) — a typical first kind superconductor having by considerable purity and crystal's perfection following superconducting characteristics: $T_C = 3.72$ K, $\Delta T_C \sim 10^{-3}$ K, $dH_C/dT \sim 12 \cdot 10^3$ A/m · K at $T$ ~ 3.5 K [3], ($T_C$-transition temperature from normal ($n$) to superconducting ($s$) state, $\Delta T_C$ — $n$-$s$ transition interval, $H_C$ — critical magnetic field).

It should be noted that Sn under $T_{\alpha\text{-}\beta}$, including liquid helium temperatures, founds practically always in a supercooled metastable modification β-Sn, which had been studying in a huge number of fundamental works on superconductivity.

The temperature dependences of electrophysical characteristics of large-size perfect β-Sn single-crystals measured from $T$ ~ 500 K in cooling mode at a speed of $v = dT/dt$ ~ 0.5 K/min, Fig. 1, show that this way the γ and $x$-Sn can not be supercooled more a few tens of degrees. This result excludes, in principle, the possibility of obtaining these modifications in large perfect single crystals at helium temperatures. As for films of vapors condensed on the substrate at $T$ = 4.2 K, they also be possessed of the crystal structure of white tin [4], but have the values of $T_C$ about 25 % higher due to the structural defects [4].

Taking into account the data of [2], as well as the fact that superconducting properties are peculiarities of the metastable supercooled modification β-Sn only, it was of interest to investigate the possibility of applying the rapid hardening method to obtain the high-temperature modifications γ- and $x$-Sn at metastable states at liquid helium temperatures in order to study the electrophysical properties ones. Below there are described experiments with Sn samples obtained during the rapid cooling of the melt overheated, and that is very important, considerably in comparison with Sn melting point ($T_{mel}$). The properties of such samples demonstrate possibility of hardening the states having electro-physical and structural anomalies in comparison with β-Sn.

## 2. Materials and measurements

To prepare the samples it was used tin of recognized analytical grade, which was characterized in the initial state by relation $\rho_{4.2\ K}/\rho_{300\ K} \approx 3 \cdot 10^{-3}$. The samples were prepared by pulling glass capillaries with liquid tin inside from glass beads of diameter $d$ ~ 3 mm containing a small amount of molten tin [5]. The Sn′ melt temperature immediately before the capillary's thread pulling exceeded the Sn′ melting point ($T_{mel} \approx 509$ K) by about (300–400) K, it is provided the necessary fluidity of glass. It is estimated that cooling rate of the capillary of diameter 0.05 mm, containing molten tin, from $T$ = (800–900) K to $T$ = 300 K is $v$ ~ $10^2$ K/sec.

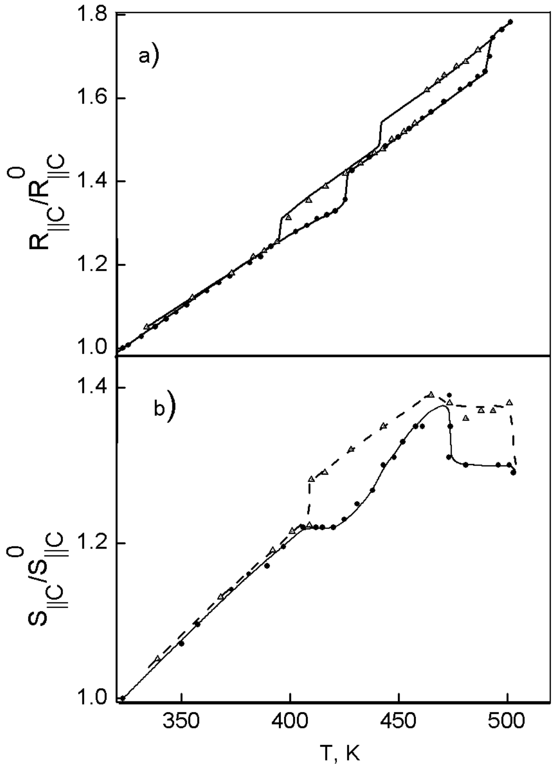


Fig. 1. Temperature dependences of normalized values of electrical resistance $R_{IIC}(T)/R^0_{IIC}$ (a) and thermo EMF $S_{IIC}(T)/S^0_{IIC}$ (b), measured along of crystallographic axis $c$ of cylindrical single-crystal β-Sn ($\rho_{4.2\ K}/\rho_{300\ K} \approx 2 \cdot 10^{-5}$, length $L$ ~ 100 mm, diameter $d$ ~ 2 mm, ρ — specific electrical resistance, $R^0_{IIC}$ and $S^0_{IIC}$ — values at $T$ = 323 K), *1* — heating, *2* — cooling [2].

The thread-like samples (filaments) of diameter $d$ ~ (0.03–0.05) mm, length $l$ ~ 20 mm, were obtained after etching up the glass shell by hydrofluoric acid. Their electrical resistance ($R$) was measured by a two-terminal configuration at first at the room temperature ($R_{300}$ K) and then in a cryostat at the liquid helium temperature ($R_{4.2}$ K). By vapor pumping the liquid helium's temperature gradually decreased at a rate of $v$ ~ $10^{-2} \div 10^{-3}$ K/min and at the same time the potential difference $U$ created between the thread ends by constant current $I$ ~ ($10^{-2} \div 10^{-4}$) A was recorded as a function of time ($t$). These data were utilized to restore dependences $U(T)$ and $R(T)/R_n$ ($R_n$ — corresponds to normal β-Sn slightly higher $T_C$). In some experiments the dependences $U(T)$ were measured directly at the points in stepped cooling regime in the quasi-stationary states. Electrical communications were soldered to the samples by the Wood's alloy,

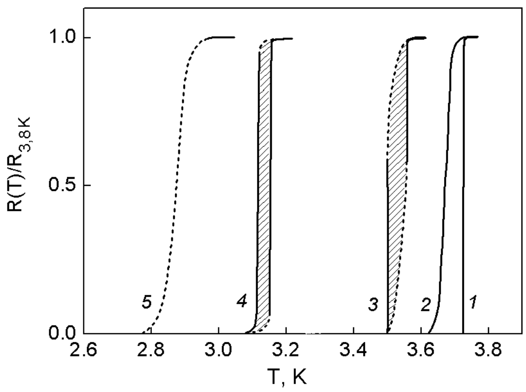


Fig. 2. Temperature dependences of normalized values of electrical resistance of Sn filaments:

*1* — β-Sn; *2* — $\rho_{4.2\ K}/\rho_{300\ K}$ ~ $1.2\cdot10^{-2}$;

*3* — $\rho_{4.2\ K}/\rho_{300\ K}$ ~ $1.2\cdot10^{-2}$;

*4* — $\rho_{4.2\ K}/\rho_{300\ K}$ ~ $1.2\cdot10^{-2}$;

*5* — $\rho_{4.2\ K}/\rho_{300\ K} \approx 15$. The regions of irregular resistance disappear are hatched.

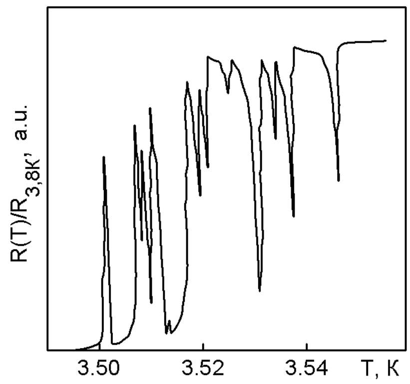


Fig. 3. Detailed picture of curve 3 from Fig. 2.

which is superconducting throughout the range of temperatures studied.

### 3. Results

Most of the samples prepared by described method had the typical β-Sn characteristics: $\rho_{4.2\ K}/\rho_{300\ K} \approx 3\cdot10^{-3}$, $T_C$ = 3.72 K, $\Delta T_C$ ~ $10^{-3}$ K and $dH_C/dT$ ~ $12\cdot10^3$ A/m·K at $T$ ~ 3 K. As indirect confirmation they had the β-Sn crystal' structure consists of the monotony of disappearance of electrical resistance in course of the *n-s* transition in zero magnetic field [6]. Such samples are not considered further.

Characteristics of the smaller group of the samples differed significantly from those of the previous ones. First of all the distinction of parameter $\rho_{4.2\ K}/\rho_{300\ K}$ was revealed: — the range of possible values were ranged from ~$10^{-2}$ to ~$10^{1}$, and it was one of the criteria of abnormality. Fig. 2–4 show the temperature dependences of the normalized resistivity of the anomalous samples at the liquid helium temperatures.

The following conclusions can be made from the data analysis:

a) $T_C$-value may be in the range from $T$ = 3.7 K to $T$ = 2.8 K, and $\Delta T_C$ value — up to ~$10^{-1}$ K, Fig. 2;

b) *n-s* transition can occur in irregular manner even in the zero magnetic field, Fig. 2, 3; the densities required of measuring current must exceeds the certain temperature depending value $J_{lim}$; for example, $J_{lim}$ ~ $4\cdot10^{-1}$ A·mm$^{-2}$ for $T$ ~ 3.3 K;

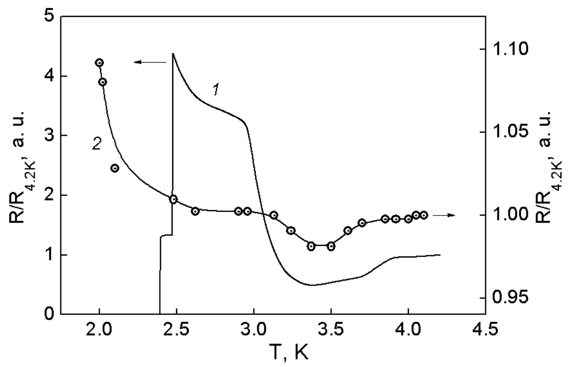


Fig. 4. Temperature dependences of normalized values of electrical resistance of Sn filaments: *1* — $\rho_{4.2\ K}/\rho_{300\ K}$ ~ $10^{-1}$, automatic registration in course of continuous cooling; *2* — $\rho_{4.2\ K}/\rho_{300\ K}$ ~ 1, registration at the points in stepped cooling regime in quasi-stationary states.

c) some samples demonstrate the coexistence of superconducting and semiconducting properties, Fig. 4. Namely: anomaly of the dependence $R(T)/R_{4.2\ K}$ in the range ~(3.9–3.4) K indicates the *n-s* transition of β-Sn, but the semiconductor section of the curve below ~3.4 K indicates that the volume portion of the sample is stored in the *n*-state. Another confirmation of the presence of someone else than β-Sn phase is the difference (about 250 times in comparison with the data of [3]) of the value of the derivative $dH_C/dT \approx 48$ A/m·K for $T$ ~ 3.3 K calculated from the experimental data. The calculation is made on the assumption of filament's homogeneity by the Silsbee formula [6] linking $H_C$ with $I_C$: $H_C = 2I_C/ca$, where $I_C$ — critical current, $c$ — electrodynamic constant, $a$ — filament's radius. To calculate the values $H_C$ at $T$ = 3.1 K and $T = 3.5$ K the measuring current's magnitudes corresponding to curves *3* and *4* on Fig. 2 were taken.

In conclusion, we point out the key detail for the results interpretation: — just after the first warming the samples from $T = 4.2$ K to $T = 300$ K they acquired the typical β-Sn electrical characteristics, in particular, parameter $\rho_{4.2\ K}/\rho_{300\ K}$ took typical for the initial tin value ~$3\cdot10^{-3}$. The latter, together with the above set of anomalies, suggests that in the process of rapid cooling the melt from $T \sim (800-900)$ K to $T = 300$ K the crystallization occurs in any metastable state allowing the supercooling down to the liquid helium temperatures and annealing to the allotropic β-Sn modification owing to heating to $T = 300$ K.

## 3. Discussion

The literature analysis showed that none of known influence methods the $T_C$ and $dH_C/dT$ of monophasic β-Sn can be reduced so much significant as described. While from the above data follows that the state of the hardened samples is not mono- but heterogeneous: the *n-s* transitions at the temperatures closed to ~3.72 K (Fig. 2) and anomaly of the dependences $R(T)/R_{4.2\ K}$ in range of ~(3.9–3.4) K, (Fig. 4), indicate that one of the hardened component is β-Sn. The semiconductor course of the curves below ~3.4 K, (Fig. 4), having, two different sections, indicates the presence, firstly, other structural components, and, secondly, that they are not superconducting. Accordingly, explanation of the conductivity anomalies of the hardened samples must be based on the taking into account the presence in the sample's volume along with superconducting phase β-Sn the phase (or phases), which is not a superconducting, i.e. on the taking into account of the well-known proximity effect in the *n-s* contacts [4].

This effect, it is known, causes a decreasing the superconducting characteristics of superconductor to the extent of the ratio of characteristic' size of the superconductor (Δ) and coherence length of Ginzburg-Landau ($\xi_{G-L}$) — up to disappearance of superconductivity at $\Delta \sim \xi_{G-L}$ [4]. In our opinion, the superconducting characteristic's anomalies observed are explained by the proximity effect namely. The proof of that is calculation by the Silsbee's formula [6] of diameter $d$ of the β-Sn monophasic filament, in which the measuring current $I$ would be critical at $R = 0$ according to our data. For example, at $T \sim 3$ K it is the current $I$, used to measuring curve *4* of Fig. 2. The value $d \sim 10^{-6}$ mm calculated this way is comparable with $\Delta \sim \xi_{G-L}$ for β-Sn [4].

Evident difference between two exponential sections of each of the dependences $R(T)/R_n$ on Fig. 4, points directly to the two-component's normal-conducting structure. It seems naturally to associate ones with the high-temperature allotropic modifications (γ- and $x$-Sn) — which are also two — recorded by measuring the electro-physical characteristics of the single crystals (Fig. 1). The reasons for this are as follows. The absence of the abnormalities in our work observed in the specimens obtained by the classical Tammann-Shubnikov-de Haas (Bridgman-Stockbarger) or Czochralski methods [7], as well as by condensation on the cooled substrates, gives reasons to believe that the key factor of the semiconductor phases hardening is the overheating the melt ~(300–400) K above $T_{mel}$. Indeed, in the classical methods [7] the temperature of melt crystallization almost equal to the temperature $T_{mel}$ of melting, because of which the quasi-lattice ordering in the melt is closed to ordering in solid [8], i.e. is tetragonal, be differing of oscillation nodes amplitudes. Cooling from $T_{mel}$ with low speed does not allow to supercoole the $x$- and γ-Sn significantly, Fig. 1.

In the case of the method used by us for the filaments manufacturing, forcibly imposed significant overheating of the melt, the situation is different. According to the existing ideas [8], quasi-lattice of liquid Sn stays tetragonal up to $T \sim (527-577)$ K, by reducing of tetragonality. Tin above $T \sim (527-577)$ K has the bcc-closed order, disappearing with the further increasing $T$ [8]. At the time of capillary pulling the liquid state of Sn, according to [8], was disordered, no doubt, but the analogy with the crystallization of the vapor on a cold substrate was not passes, judging from the increasing $T_C$ of film [4]. On this base the semiconductor states detected can be associated with the hardened allotropic modifications γ- and $x$-Sn.

## 4. Conclusions

We studied the low-temperature electrical properties of Sn-filaments with diameter $d \sim (0.03-0.05)$ mm, hardened during cooling of the melt at the rate of $\upsilon \sim 10^2$ K/sec from $T \sim (800-900)$ K to $T = 300$ K. For the first time at the liquid helium temperatures the anomalies were detected indicating the presence in solid state of allotropic modification of β-Sn in mixture with two semiconductor phases, which are not superconducting at least down to $T$ ~ 2.5 K. It is suggested to identify the semiconducting phases with supercooled metastable allotropic modifications of Sn, which exist in equilibrium states above $T$ ~ 430 K. The superconducting anomalies are explained by the proximity effect. The complex morphology of the hardened state is, apparently, the consequence of the high disordering of Sn′ melt before hardening.

## References


1. Fizicheskaya Enciklopediya, ed. by A.M.Prokhorov, Sovetskaya enciklopediya, Moscow (1988) [in Russian],
2. V.I.Sokolenko, V.A. Frolov, *Probl. Atomic Sci. Techn. Ser. "Vacuum, Pure Mater. Supercond."*, **6(19)**, 195 (2011).
3. J.M.Lock, A.B.Pippard, D.Shonberg, *Proc. Camb. Phil. Soc.*, **47**, 811 (1951).
4. W.Buckel, Supraleitung, Physik Verlag GmbH (1972).
5. A.A.Galkin, B.G.Lazarev, *Doklady Akademii Nauk SSSR*, **61**, 1017 (1948).
6. A.C.Rose-Innes, E.H.Rhoderick, Introduction to Superconductivity, Pergamon Press (1969).
7. R.Lodiz, R.Parker, Rost Kristallov, Mir, Nauka, Moskow, (1974) [in Russian].
8. V.K.Grigorovich, Metallicheskaya Svyaz i Structura Metallov, Nauka, Moskow, (1988) [in Russian].