INVESTIGATION OF TUNNEL CHARACTERISTICS OF SPUTTERED SUPERCONDUCTING Nb_3Sn FILMS

S. I. VEDENEEV, A. I. GOLOVASHKIN, I. S. LEVCHENKO and G. P. MOTULEVICH

P. N. Lebedev Physics Institute, USSR Academy of Sciences

Submitted March 28, 1972

Zh. Eksp. Teor. Fiz. 63, 1010–1019 (September, 1972)

We investigated the tunnel characteristics of sputtered superconducting Nb_3Sn films with $T_c = 17.8–18.3°K$ of thickness 0.3–2.0 μ. The I–V characteristics and the $dI/dV = f(V)$ plots were obtained for Nb_3Sn-Pb and Nb_3Sn-Sn tunnel junctions. The tunnel barrier was either an oxide layer on the surface of the electrically polished Nb_3Sn film or a layer of aluminum oxides. Four values of the Nb_3Sn energy gap are obtained, each of which is much smaller than follows from the theory, while the tunnel density of states has a complicated structure. An anomalously low energy gap was observed for Nb_3Sn, namely $2\Delta/e = 0.36$ mV. The results are discussed from the point of view of the energy-gap anisotropy in Nb_3Sn.

INTRODUCTION

ONE of the most promising superconducting alloys is Nb_3Sn, which has high critical parameters and is successfully used in a number of superconducting devices[1,2]. So far, however, its electronic and acoustic characteristics are not sufficiently well known, and the reason for such a high critical temperature is not fully clear. The published data are contradictory even with respect to such a fundamental characteristic of this superconductor as the energy gap. Different methods give significantly different results. The data of the tunnel experiments[3-7] deviate strongly from the results of the measurements of the specific heat[8], thermal conductivity[9], infrared absorption[10], and luminescence[11]; even the results obtained by the tunnel method are not in agreement.

The mean free path l and the coherence length ξ of the alloy Nb_3Sn are of the order of 100 Å[1]. It is therefore very important for tunnel experiments that the properties of the surface layer of such thickness coincide with the properties of the bulk material. In addition, since experiments show that the current-voltage characteristics of tunnel junctions with Nb_3Sn have a complicated structure, a high apparatus resolution is required for their analysis. Either one of these conditions or both were not fulfilled in the earlier investigations[3-7].

We have investigated the tunnel characteristics of sputtered Nb_3Sn films whose properties coincided with the properties of the bulk material. The sensitivity and the resolution of the apparatus have made it possible to obtain a detailed analysis of the current-voltage characteristics of the investigated films.

EXPERIMENTAL DETAILS

1. The tunnel characteristics were measured on Nb_3Sn-Pb and Nb_3Sn-Sn film tunnel junctions. The procedure for preparing the Nb_3Sn films was described earlier[12]. By choosing more carefully the evaporation and heat-treatment conditions and by coming closer to stoichiometry than in[12], we were able to obtain samples that become superconducting at $T_c = 17.8–18.3°K$, with a transition with $\Delta T = 0.1–0.3°K$. T_c was measured by a null method and was taken to mean the temperature corresponding to half the residual resistance. The temperature was measured accurate to 0.01°K with a TSPN-1 platinum thermometer and a TSJ-1 germanium thermometer. The measurements of T_c were made immediately after the sputtering of the Nb_3Sn film, as well as after the end of the tunnel measurements.

X-ray studies of the obtained Nb_3Sn films have shown that they have an A-15 structure. No other phases were observed. The lattice constant was $a = 5.31 \pm 0.02$ Å, in good agreement with the lattice constant of bulk samples[1]. The thicknesses of the Nb_3Sn films were determined by an interference method and amounted to 0.3–2.0 μ. The resistance ratio was $R_{300°K}/R_{res} = 1.5–3.5$, where $R_{300°K}$ and R_{res} are respectively the room and residual temperatures.

2. To prepare the tunnel junctions, the Nb_3Sn films were deposited first on a polished ruby substrate in the form of narrow strips 1–3 mm wide and 10–70 mm long. The tunnel barrier was either an oxide layer on the surface of the Nb_3Sn film or a layer of aluminum oxide approximately 50 Å thick. The second film was evaporated Pb or Sn, the tunnel characteristics of which were investigated beforehand[13]. The area of the tunnel junction was 1–3 mm^2. As a rule, three to seven tunnel junctions were obtained in one sample (Fig. 1).

The same tunnel junction could be investigated many times for several days, with intermediate heating to room temperature. In addition, it was possible to wash off the Pb and Sn films several times and deposit new ones on the same Nb_3Sn strip.

The ruby substrate with the tunnel junctions was placed in a special holder, in which indium current-conducting strips were clamped to the current and potential contacts.

3. The preparation of good tunnel junctions with Nb_3Sn entails great difficulties, because "microwhiskers"[1] are produced on its surface and lead to "microshorts" and "microbridges" through the dielec-

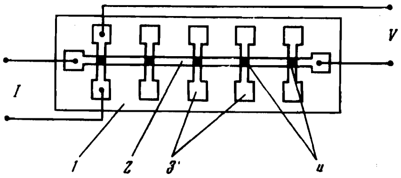

FIG. 1. Diagram of tunnel junctions: 1—ruby substrate; 2—Nb_3Sn film; 3—Pb or Sn film; 4—tunnel junction.

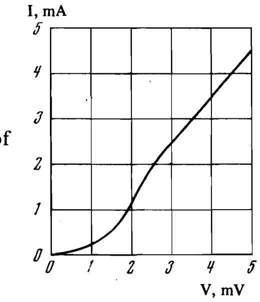

FIG. 2. Current-voltage characteristic of Nb_3Sn-Pb tunnel junction at T = 2.2°K.

tric layer[1)]. If the transition of the microshort to the normal state occurs quite abruptly at currents falling in the working interval, then the tunnel current-voltage characteristics (I-V characteristics) become strongly distorted, so that it is impossible to determine the energy gap exactly[2)]. Scidel and Wicklund[3] determined the Nb_3Sn gap incorrectly because they used such distorted I-V characteristics.

We were able to get rid of the microshorts by electrolytically polishing the Nb_3Sn films in a mixture of 10% HF, 40% HNO_3, and 50% H_2SO_4 diluted in water. The polished sample served as the anode, and the cathode a graphite plate. The optimal electrode voltage was 6—8 V. The thickness of the removed layer was determined from the change of the film resistance. The removed layer amounted to 10—30% of the total film thickness. Such polishing conditions preserve the mirror finish of the surface and make it possible to obtain good tunnel junctions[3)]. After the polishing, the films were exposed to air for several hours, to produce on their surface a uniform oxide layer of the required thickness. Most investigated junctions were prepared in this manner.

In addition to the indicated method, we were able to obtain in a number of cases good tunnel junctions without electrolytically polishing the Nb_3Sn films[4)]. The tunnel barrier was either a specially deposited layer of aluminum oxide or the oxide layer on the Nb_3Sn surface. The aluminum-oxide layer had a total thickness of approximately 50 Å. It was prepared by repeated evaporation of aluminum layers ~ 10 Å thick followed by oxidation of each layer in air.

The oxide layer was produced on the unpolished Nb_3Sn samples either by heating the films to 100—200°C in air, or in an oxygen atmosphere at atmospheric pressure and at a pressure 5×10^{-1} mm Hg, or else by oxidation in an oxygen discharge.

The resistance of good tunnel junctions prepared by different methods was 0.1—2 Ω/mm^2. In some cases, junctions with weak microshorts were used to investigate the singularities of the I-V characteristics at low voltages. The junction resistance in this case amounted

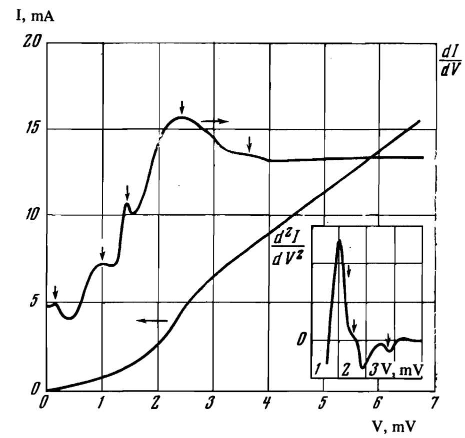

FIG. 3. I—V characteristic and dependence of dI/dV on V for an Nb_3Sn-Pb tunnel junction T = 1.9°K. The insert shows separately a plot of d^2I/dV^2 against V in the interval 1.6—5.0 mV.

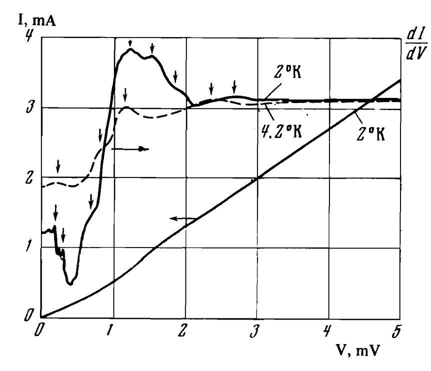

FIG. 4. I-V characteristic and dependence of dI/dV on V for an Nb_3Sn-Sn tunnel junction. The dashed curve (T = 4.2°K) corresponds to an S-N tunnel junction.

to ~ 0.01 Ω/mm^2. The results obtained for tunnel junctions with different dielectrics agreed with one another.

4. We measured the I-V characteristics and the dependence of dI/dV on the voltage V with a previously described setup[13] (dI/dV and d^2I/dV^2 are shown in all the figures in arbitrary units). The I-V characteristics of the investigated tunnel junctions had the "classical" form (Fig. 2). These characteristics, however, contained singularities (Figs. 3 and 4), which are marked by arrows in the figures. To study each singularity in the corresponding voltage interval, we adjusted individually the modulation signal level and the amplifier gains. Measures were taken to reduce the induced noise. To determine more precisely the shape of the

[1)]The "microwhiskers" have apparently the structure of ideal crystals. The conditions for their formation on the surface are favorable during the evaporation.

[2)]It should be noted that microshorts of the microbridge type produce little distortion in the I-V characteristics of tunnel junctions, and make it possible to observe more clearly the singularities at low voltages [13,14].

[3)]Usual chemical etching only makes the surface properties worse, without removing the microshorts.

[4)]These films were subsequently also polished electrolytically. Results of the tunnel experiments were fully identical in both cases.

dI/dV curve, we obtained the plot of d^2I/dV^2 against V in some cases. To this end, a frequency doubler was added to the reference-signal circuit of the employed synchronous detector.

The tunnel characteristics were measured at different temperatures from 1.9 to 20° K.

RESULTS

1. We investigated more than 100 tunnel junctions on 26 Nb_3Sn films. The results revealed the presence of a strong singularity on the I-V characteristic of the investigated tunnel junctions (see Fig. 2). The maximum of the derivative dI/dV, corresponding to this main singularity, lies at V = 2.1—2.4 mV and V = 1.2—1.5 mV for Nb_3Sn-Pb and Nb_3Sn-Sn tunnel junctions, respectively (Figs. 3 and 4).

With increasing temperature, the main maximum of dI/dV becomes smeared out and shifts towards lower voltages (Fig. 5). At a temperature exceeding the temperature of the superconducting transition of Pb or Sn, the abrupt singularity on the I-V characteristic of the tunnel junction disappears. There remains a smooth singularity corresponding to a broad maximum on the dI/dV = f(V) curve in the region V = 1—1.5 mV. All the singularities on the current-voltage characteristic disappear at T > 18° K.

2. An analysis of the results has shown that the I-V characteristics have in the 0—4 mV region eight singularities corresponding to maxima on the dI/dV = f(V) curves. No noticeable singularities were observed in the 4—7 mV region.

The main maximum of the derivative, corresponding to the abrupt increase in the current on the I-V characteristic, turns out to be a double maximum, as seen from Fig. 4. In the case of the junction with Pb, this maximum can likewise always be resolved into components, but this requires either the use of the second derivative (Fig. 3) or a strong decrease of the level of the modulation signal (Fig. 6).

3. On the high-voltage edge of the indicated double maximum of dI/dV there is a maximum at V = 3.5—3.7 mV for the Nb_3Sn-Pb junction and at V = 2.7—2.8 mV for the Nb_CSn-Sn junction (Figs. 3, 4, and 6). The optimal conditions for its observation coincide with the conditions for separating the two preceding maxima.

All three maxima overlap strongly and are component parts of one main maximum.

4. The next clearly noticeable singularity on the I-V characteristic and a distinct maximum of dI/dV are observed in the 1.4—1.6 mV region for the Nb_3Sn-Pb junction and 0.6—0.7 mV region for the Nb_3Sn-Sn junction (Figs. 3 and 4). Separation of this maximum entails no difficulty. It appears on all the curves together with the main maximum of dI/dV. The maximum is particularly clearly seen in the case of junctions with weak microshorts, in the region 0.6—0.7 mV (Fig. 7).

The temperature dependence of the indicated singularity of the I-V characteristic coincides with the temperature dependence of the main singularity, as seen from Fig. 5.

5. A broad maximum of complicated shape is observed for the Nb_3Sn-Pb tunnel junction in the region 0.5—1.2 mV (Fig. 3). By increasing the voltage sensitivity of the circuit when measuring the dependence of dI/dV against V it is easy to resolve this maximum into two maxima, at V = 0.5—0.7 mV and V = 0.9—1.2 mV (Fig. 8). We see that the shape of the second maximum remains complicated, and a thorough analysis of the temperature dependence shows that it is double maximum. The stronger maximum of these two lies in the region V = 1.1—1.2 mV. The second, which is much weaker than the first, is located at V = 0.9—1.0 mV.

The same Fig. 8 shows clearly the maximum at V ≈ 0.1—0.2 mV. This maximum is well observed at low temperatures on all the dI/dV = f(V) curves.

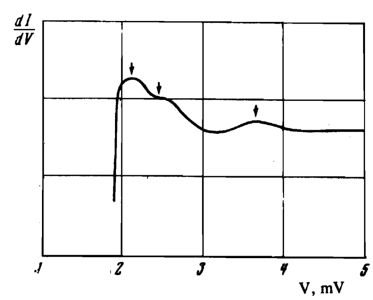

FIG. 6

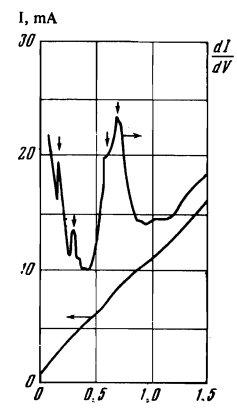

FIG. 7

FIG. 6. Dependence of dI/dV on V for an Nb_3Sn-Pb tunnel junction at T = 4.2°K in the 1—6 mV range.

FIG. 7. I-V characteristic and dependence of dI/dV on V at low voltages for an Nb_3Sn-Sn tunnel junction with a microbridge (T = 2.0°K).

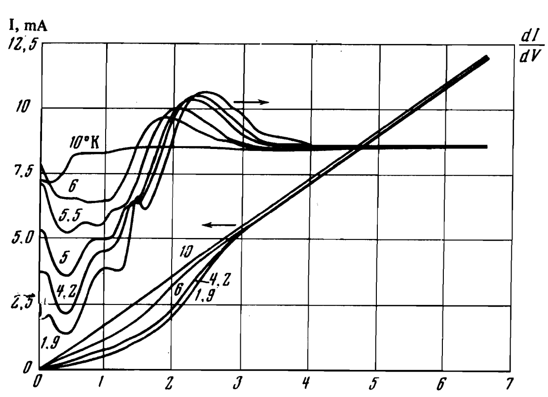

FIG. 5. I-V characteristics and dependence of dI/dV on V for an Nb_3Sn-Pb tunnel junction at different temperatures.

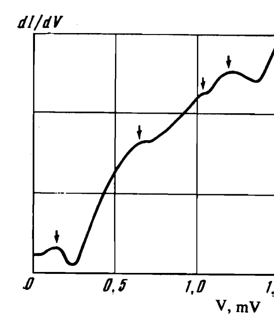

FIG. 8. Dependence of dI/dV on V for an Nb_3Sn-Pb tunnel junction in the range V = 0—1.5 mV at T = 1.9°K.

6. For the Nb_3Sn-Sn tunnel junction one observes at low voltages a rather complicated picture. The derivatives show distinct maxima in the regions V = 0.2 and V = 0.3 mV, and a weak maximum at V = 0.5—0.6 mV is observed near the sharp maximum at V = 0.6—0.7 mV. These maxima appear on all the curves. They are seen most distinctly, however, for junctions with weak microshorts (Fig. 7).

In addition to the indicated maxima, a singularity is observed near V = 1.7—1.9 mV on the dI/dV = f(V) curves for the Nb_3Sn-Sn junctions; this singularity can be well separated only with the aid of the second derivative.

7. Measurements were made also on tunnel junctions of the S – N type, in which the second metal (Pb or Sn) was in the normal state. By way of example, Fig. 4 shows a plot of dI/dV against V for an Nb_3Sn-Sn junction. The positions of the maxima on such curves are directly connected with the energy gaps of Nb_3Sn.

8. All the experimental dI/dV = f(V) curves were normalized to unity in the region 5—7 mV. Figures 9 and 10 shows the common $(dI/dV)_{norm}$ curves, plotted from the results obtained in each of the voltage regions indicated above. With such a normalization, the curves in Figs. 9 and 10 reflect the combined tunnel density of states of the Nb_3Sn-Pb and Nb_3Sn-Sn junctions. The complicated character of the curves indicates that Nb_3Sn has several energy gaps.

9. If we disregard the complicated character of the observed curves, then the sharp singularity on the I-V characteristic (Fig. 2) and the corresponding principal maximum of the derivative dI/dV at V ≈ 2.4 mV for the Nb_3Sn-Pb junction (Fig. 9) and at V = 1.4 mV for the Nb_3Sn-Sn junction (Fig. 10) can be related only to the sum of the energy gaps of the two superconductors making up the tunnel junction[14,15]. Using the known values of the energy gaps of Pb and Sn[13-17], we easily obtain the effective value of the energy gap for Nb_3Sn, namely, $2\Delta_{eff}/e \sim 2$ mV, corresponding to a ratio $2\Delta_{eff}/kT_c \approx 1.3$.

10. From Figs. 9 and 10 we see clearly that the dI/dV = f(V) curves of tunnel junctions with Nb_3Sn have eight maxima, which can be easily broken up into four pairs corresponding to the sum and difference of the gaps of Nb_3Sn with the gap of Pb or Sn. The indicated breakup into pairs was carried out for each experimental curve. From the sum and difference we determined the gaps of Nb_3Sn and Pb or Sn. We then averaged over all the samples and all the junctions. The results obtained for different samples were in good agreement. The values obtained for Pb and Sn were $2\Delta_{Pb}/e = 2.66 \pm 0.03$ mV and $2\Delta_{Sn}/e = 0.94 \pm 0.02$ mV, in good agreement with the gaps of Pb and Sn at T ≈ 2° K, measured by us earlier[13], and with the published data[14,17].

For Nb_3Sn we obtained the following four values of the gap and of the ratio $2\Delta_{Nb_3Sn}/kT_c$:

$2\Delta_{Nb_3Sn}/e$, мв:	4,70±0,04	2,24±0,04	1,50±0,04	0,36±0,04
$2\Delta_{Nb_3Sn}/kT_c$:	3,0	1,4	1,0	0,2

(e is the electron charge). Since the temperature at which the measurements were made is almost one-tenth the value of T_c of Nb_3Sn, the indicated values of Δ for Nb_3Sn can be regarded as corresponding to T = 0° K.

DISCUSSION OF RESULTS

1. We obtained four values of the energy gap of Nb_3Sn. It is seen from Figs. 9 and 10 that the main tunnel density of states is connected with the gaps Δ_2 and Δ_3 in Nb_3Sn. The tunnel density of states connected with the gaps Δ_1 and Δ_4 is much smaller.

In earlier tunnel experiments with Nb_3Sn there was observed only one gap[3-5] $2\Delta/e \sim 2$ mV, which agrees well with the effective value of the gap obtained by us.

The only tunnel experiment performed on a polycrystalline Nb_3Sn sample[6] yielded $2\Delta/e = 5.6$ mV. Unlike the earlier investigations, a point tunnel junction with very large resistance was used in[6]. However, much lower values of 2Δ, coinciding with our results, were obtained for Nb_3Sn single crystals in[7], where the same measurement method was used.

2. We see that all ratios $2\Delta_{Nb_3Sn}/kT_c$ given above are much smaller than the value 3.5 that follows from the BCS theory[18]. The small Δ of Nb_3Sn is attributed[1,4,7] to possible changes of Δ near the sample boundary. Such a change of Δ can occur if the electron mean free path is small and the surface layer is distorted when the sample surface is worked. Earlier tunnel experiments left the question of the influence of the sample surface on the smallness of Δ open, since l was either unknown or pertained to the bulk sample, while the sample surface was worked and the distortion of the surface layer was not controlled.

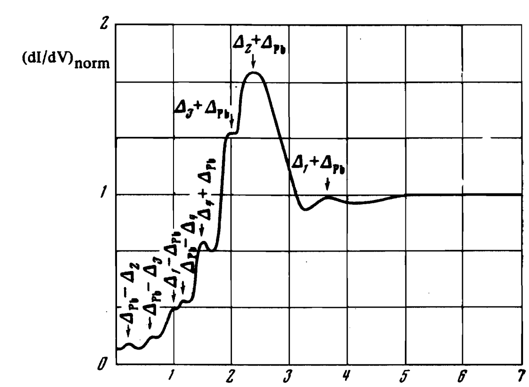

FIG. 9. Normalized common plot of $(dI/dV)_{norm} = f(V)$ for Nb_3Sn-Pb junction. The arrows mark the positions of the sum and difference of the Nb_3Sn gaps (Δ_1, Δ_2, Δ_3, Δ_4) and of the Pb gap (Δ_{Pb}).

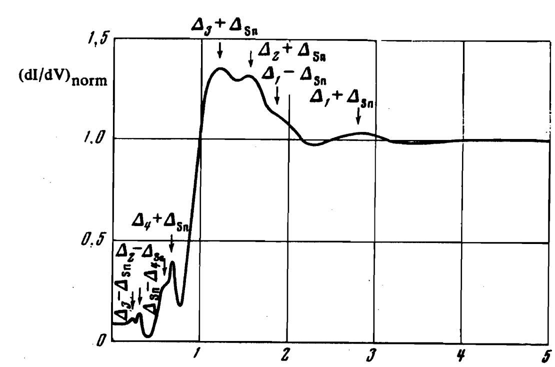

FIG. 10. Normalized common curve $(dI/dV)_{norm} = f(V)$ for the Nb_3Sn-Sn junction. The arrows mark the positions of the sum and difference of the gaps of Nb_3Sn (Δ_1, Δ_2, Δ_3, Δ_4) and the gap of Sn (Δ_{Sn}).

The samples investigated by us had[5)] $l \sim 100$ Å. Their preparation method excluded any distortion of the surface layer. In addition, identical results were obtained for both freshly evaporated and for electrically polished samples. Thus, the small $2\Delta/kT_c$ of Nb_3Sn cannot be attributed to a change of Δ near the sample boundary.

3. We observed an anomalously small gap of Nb_3Sn, namely $2\Delta_4/e = 0.36$ mV, which was previously not observed for Nb_3Sn. The curves obtained by us give grounds for assuming that the anomalously small gap of Nb_3Sn has a complicated structure (several small gaps possibly exist). The resolution of this structure, however, is at present beyond the accuracy limits of our measurements. We note that the presence of an anomalously small gap in Nb_3Sn is not unexpected, since Nb has a second gap much smaller than the main gap[20].

The observed gap Δ_4 cannot belong to pure Nb. It is somewhat larger than the small gap of pure Nb. Furthermore, the Debye grams of our samples have shown that they contain only one Nb_3Sn phase with A-15 lattice, and there are no traces of the lattice of pure Nb. Finally, two energy gaps (3.1 and 0.30 mV) were observed in pure Nb. In none of our tunnel experiments did we observe even the main gap of Nb. Thus, the anomalously small gap found by us belongs to the Nb_3Sn compound with the A-15 lattice.

4. We assume that the presence of several values of Δ is due to the anisotropy of the Nb_3Sn gaps. A similar conclusion was drawn by Hoffstein and Cohen[7], who performed tunnel investigations of Nb_3Sn single crystals, and also by Weger[21], who presented a theoretical interpretation of the results of[7]: Gap anisotropy was observed in[7] in the interval $2\Delta/e = 1.5$–4.4 mV, in good agreement with our results for Δ_1, Δ_2, and Δ_3.

Assuming a uniform distribution of the crystals in the Nb_3Sn film (this is confirmed by x-ray tests), we can suppose that the $dI/dV = f(V)$ curves give a tunnel state density that is averaged over all directions. The data demonstrate that the state density is maximal in the region of the second and third gaps (1.5–2.2 mV) and that there is a small maximum in the 4.7 mV region. The anomalously small gaps are apparently second gaps in each direction.

The foregoing interpretation is not the only one possible. The phonon spectrum of Nb_3Sn has not been investigated and may exert a definite influence on the observed picture in some cases. In addition, an additional weak singularity was observed in certain Nb_3Sn samples in the region of the main maximum of dI/dV, which may be evidence of a still more complicated structure of the tunnel state density.

5. There are presently several known papers in which the gap of Nb_3Sn was obtained by other methods[8-11]. The authors obtained a ratio $2\Delta/kT_c$ close to the theoretical value. In our opinion, the experimental data was not reduced quite correctly in either of these investigations. No account was taken of the existence of a set of energy gaps, which follows from the tunnel experiments. However, a discussion of the results of these investigations is beyond the scope of the present article.

In the reduction of the experimental dependences of dI/dV on V we used only the positions of the maxima, which made it possible to determine the energy gaps of Nb_3Sn. In addition, significant information is contained also in the complete form of the $dI/dV = f(V)$ curve. However, the use of this information calls for a more detailed theoretical analysis.

[5)] l was determined by using the results of optical measurements [19] and of measurements of the static conductivity of the investigated samples.

[1] In: Sverkhprovdyashchie soedineniya niobiĭ-olovo (Superconducting Niobium-Tin Compounds), Metallurgiya, 1970.

[2] N. E. Alekseevskiĭ, Usp. Fiz. Nauk **95**, 253 (1968) [Sov. Phys.-Uspekhi **11**, 403 (1968)]. A. Echarri and M. Spadoni, Cryogenics, No. 8, 274 (1971).

[3] T. Scidel and A. M. Wicklund, Proc. 8-th Intern. Conf. of Low Temp. Phys., London, 1962.

[4] Y. Goldstein, Rev. Mod. Phys. **36**, 213, 1964.

[5] C. A. Neugebauer, J. Appl. Phys. **35**, 3599, 1964.

[6] H. J. Levinstein and J. E. Kunzler, Phys. Lett. **20**, 581, 1966.

[7] V. Hoffstein and R. W. Cohen, Phys. Lett. **29A**, 603, 1969.

[8] L. J. Vieland and A. W. Wicklund, Phys. Rev. **166**, 424, 1968.

[9] G. O. Cody and R. H. Cohen, Rev. Mod. Phys. **36**, 121, 1964.

[10] D. R. Bosomworth and G. W. Cullen, Phys. Rev. **160**, 346, 1967.

[11] L. M. Fraas, P. F. Williams and S. P. S. Porto, Solid. St. Comm., 8, 2113, 1971.

[12] A. I. Golovashkin, I. S. Levchenko and G. P. Motulevich, Fiz. Met. Metallov. **33**, 1213 (1972).

[13] S. I. Vedeneev, A. I. Golovashkin and G. P. Motulevich, Kratkie soobshch. po fizike (FIAN), No. 4, 15 (1972).

[14] D. H. Douglass and L. M. Falicov, Superconductivity (Russ. transl.), Nauka, 1967.

[15] E. Burstein and S. Lunqvist, Tunneling Phenomena in Solids, New York, 1969.

[16] J. Giaever and K. Megerle, Phys. Rev. **122**, 1101, 1961.

[17] In: Superconductivity, 1, New York, 1969.

[18] J. Schrieffer, Theory of Superconductivity, Benjamin, 1964.

[19] A. I. Golovashkin, E. D. Donner, I. S. Levchenko and G. P. Motulevich, Zh. Eksp. Teor. Fiz. **59**, 1967 (1970) [Sov. Phys.-JETP **32**, 1067 (1971)]; FIAN Preprint No. 6, 1971.

[20] J. W. Hafstrom and M. L. A. MacVicar, Phys. Rev. **2B**, 4511, 1970.

[21] M. Weger, Solid St. Comm., **9**, 107, 1971.

Translated by J. G. Adashko
107