OPTICAL PROPERTIES AND ELECTRONIC CHARACTERISTICS OF ALLOYS OF NIOBIUM WITH TIN

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Submitted June 7, 1970

Zh. Eksp. Teor. Fiz. 59, 1967–1974 (December, 1970)

An optical method was used to investigate the electronic characteristics of Nb-Sn alloys. In the same samples, we measured the complex refractive index in a spectral interval 1—10 μ, the superconducting characteristics, and also the density, the static conductivity, and its dependence on the temperature. The main investigations were performed for alloys with Sn concentrations from 6 to 55 wt.%. We determined the conduction-electron concentration, the velocity of the electrons on the Fermi surface, the total area of the Fermi surface, the effective electron-collision frequency, the frequencies of the electron-phonon and electron-defect collisions, the electron mean free path, and the skin-layer depth. The correlation between the conduction-electron concentration and the superconducting-transition temperature is considered.

INTRODUCTION

THE present paper is a continuation of investigations, by an optical method, of the electronic characteristics of alloys possessing a lattice of the type A-15 (β-W). In the earlier investigations[1-4] we studied in detail alloys of V with Ga. We describe here the results of investigations of alloys of Nb with Sn. The interest in these alloys is due to their high critical superconducting parameters. At the present time these alloys have the largest T_c and H_c of all the two-component systems (T_c is the temperature of the superconducting transition and H_c is the critical magnetic field)[5,6].

SAMPLES

1. We prepared samples of Nb-Sn alloys containing from 5 to 72 wt.% of Sn[1]. The relative error in the determination of the Sn content was ~7% for samples with low tin content, 5% for compounds close to stoichiometric, and 3—4% for samples with large tin content. The samples were prepared by sputtering in vacuum on polished substrates of sapphire, ruby, and quartz. The investigated layers had mirror surfaces, making it possible to investigate their optical properties. Samples with thicknesses from 0.1 to 1 μ were prepared (to investigate the dependence of the parameters on the thickness, thinner layers of the alloy were also prepared).

In addition to the optical constants, we measured the following characteristics of the samples: 1) superconducting characteristics—T_c, density of the critical current j_c, and width ΔT of the interval of transition to the superconducting state; 2) static characteristics—density ρ, static conductivity σ_{st} and its dependence on the temperature T, and residual resistance R_{res}.

2. T_c and ΔT were measured by a resistive method; the transition temperature was assumed to correspond to $R = R(T_c) = R_n/2$, where $R(T)$ is the resistance of the sample at the temperature T and R_n is the resistance of the sample in the normal state before the start of the transition. (In most cases $R_n = R_{res}$.) When the temperature was lowered below T_c, the sample resistance dropped to zero.

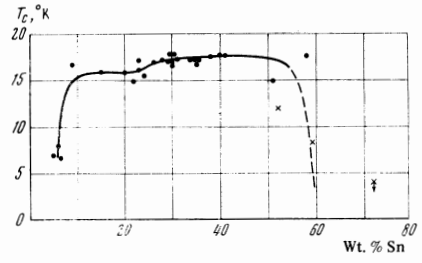

FIG. 1. Dependence of T_c on the composition of the Nb-Sn alloy. The arrow indicates that the alloy having this composition does not become superconducting down to T = 4.2°K.

The dependence of T_c on the composition is shown in Fig. 1. The crosses in this figure and in the following ones correspond to samples (with large tin contents) not subjected to heat treatment. It is seen from the figure that a large value of T_c is maintained in a large composition interval[2]. The maximum T_c was obtained for two alloys containing 30% Sn, and equaled 17.8°K. However, the value of T_c averaged over many samples (equal to 17.2°K for an alloy with 30% Sn) increased somewhat when the Sn content was increased to 40%, and amounted to 17.6°K. Alloys containing 70° Sn were not superconducting down to 4.2°K. We note that the transition to the superconducting state in samples with T_c = 17.8°K began at T = 18.1°K. The dependence of T_c on the composition is similar to the corresponding curve for the V-Ga alloy[1-4].

The width ΔT of the transition interval ranged from 0.08 to 1.5°K. The average of ΔT for alloys with compositions close to stoichiometric was ~0.5°K.

[1]The alloy compositions are indicated throughout in percent by weight. The stoichiometric composition Nb_3Sn corresponded to an alloy containing 29.9 wt.% Sn.

[2]The presence of a "plateau" in the concentration dependence of T_c was observed also in [7,8] for samples obtained by other methods. The concentration-variation interval in these investigations was smaller.

The values of T_c and ΔT for the investigated alloys were practically independent of the film thickness d at $d \gtrsim 0.1\ \mu$. For example, for alloys with 30–40% Sn, the temperature T_c started to decrease, and ΔT started to increase, at $d < 0.09\ \mu$, reaching values $T_c = 16.4°K$ and $\Delta T \approx 2°K$ at $d = 0.06\ \mu$[3]. For comparison, we note that cast samples of Nb_3Sn have T_c in the interval from 17.6 to 18.1°K[5-7,9]. At compositions far from stoichiometric, the maximum attained temperature was 18.2°K[8,9].

The critical current density j_c (in a zero magnetic field) ranged from 1×10^5 to 8×10^5 A/cm^2. On the average, samples with large T_c had also large j_c.

3. The density was determined by weighing the layer and measuring its thickness and area. The thickness was measured by interferometry.

The density ρ of our layers depended little on the composition. For alloys containing 25–45% Sn it equaled 8.9 g/cm^3. When the Sn content was decreased to 7%, the density dropped to 8.4 g/cm^3. The rms error in the determination of the density was 4%. For the intermetallic compound Nb_3Sn, the density calculated from the lattice constant is 8.92 g/cm^3[8,9].

The static conductivity σ_{st} at room temperature was determined by the usual method. Its dependence on the composition is shown in Fig. 2. The rms error of the determination of σ_{st} amounts, depending on the composition, to 5–10%.

The ratios R_N/R_r and R_{res}/R_r (where R_N and R_r are respectively the sample resistances at 78°K and 293°K) had a relatively large scatter as a function of the composition, but on the average their dependence was approximately linear. For an alloy with 5% Sn we obtained $R_N/R_r = 0.72$ and $R_{res}/R_r = 0.68$, while for an alloy with 72% Sn we got $R_N/R_r = 0.43$ and $R_{res}/R_r = 0.12$. The rms errors of these quantities ranged from 5 to 10%.

An attempt was made to observe a phase transition in the region 30–40°, such as is observed in cast single crystals[10]. For a sample with 30% Sn, we measured the dependence of the resistance on the temperature in the region $T_c < T \leq 78°K$. No singularities were observed. The sensitivity to the change of the resistance was ~0.1%.

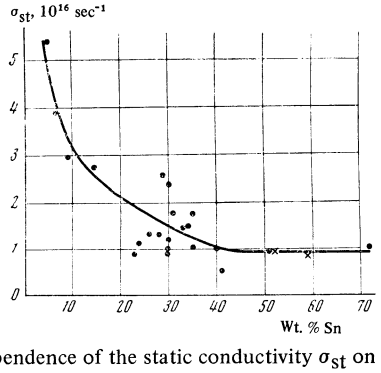

FIG. 2. Dependence of the static conductivity σ_{st} on the composition of the Nb-Sn alloy.

[3]We note that even a sample 0.03μ thick, containing 23% Sn, had a sufficiently high value of T_c (~15°K). The value of ΔT for this sample was ~2°K.

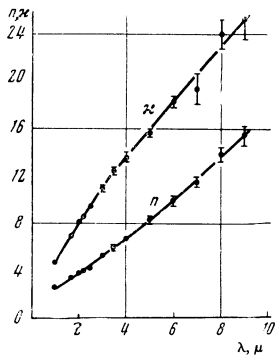

FIG. 3. Dependence of n and κ on λ for an alloy containing 30% Sn. The points indicate the experimental values and the solid line the averaged curve. The measurement errors are indicated in the figure.

OPTICAL PROPERTIES

Measurements of the optical properties of the Nb-Sn alloys were made by a polarization method using the setup described in[11,12]. We investigated samples with the following average compositions: c = 6, 22, 28, 30, 34, 40, 55 wt.% Sn. For the samples with 6, 22, 28, and 30% Sn we used reflection of light from four investigated samples. For the remaining compositions we used two reflections from the investigated samples and two reflections from standard mirrors. The deviation $\Delta c/c$ from the average composition did not exceed 10% for individual samples. It amounted to ~13% only for the samples with 6% Sn. For compositions with 30–40% Sn, this deviation equaled 1–3%.

The measurement results obtained after averaging are listed in Table I. Figure 3 shows by way of an example plots of n and κ ($n - i\kappa$ is the complex refractive index) against the wavelength λ of the light for the alloy with 30% Sn. The experimental points and the measurement errors of individual points are indicated. The monotonic dependence n and κ on λ in a wide region of the spectrum, and also the inequality $\kappa > n$, offer evidence that the dispersion of the optical constants of the alloy has a metallic character.

The character of the dependence of the reflectivity R of the Nb-Sn alloys on λ is similar to the corresponding curves for V-Ga alloys[4]. In the region $\lambda \approx 6-10\ \mu$ the value of R reached 92–93% for the alloy with 30% Sn.

DETERMINATION OF ELECTRONIC CHARACTERISTICS

The electronic characteristics were determined by the method proposed in[1,2]. We chose a spectral interval in which the dependence of $1/\sigma$ on ω^2 was linear. Here σ is the conductivity at the cyclic frequency ω. The parameters of the obtained dependence make it possible to determine the conduction-electron concentration N and the effective electron-collision frequency ν by means of formulas (5)–(7) of[1]. It turned out that $1/\sigma$ varied linearly with ω^2 for all alloys in the long-wave region of the spectrum. We used a single spectral interval 5–8 μ for all the compositions. The determined electronic characteristics are listed in Table II. Here N_a—concentration of the atoms, N_{val}—concentration of the valence electrons, v_F—average velocity of the electrons on the Fermi surface, v_F^0—velocity of the free electrons on

Table I. Optical constants of Nb-Sn alloys

λ, μ	Wt. % Sn													
	6		22		28		30		34		40		55	
	n	×	n	×	n	×	n	×	n	×	n	×	n	×
1.0	2,4	4.6	3,1	4.5	2,8	4,3	2,65	4,75	2,9	3,45	2,6	2,35	3,2	3,3
1.25	2.7	5.5	3,35	5,0	2,9	5,4	2,9	5,6	3,0	3,95	2.5	2,55	3,3	3,6
1.5	2.95	6.6	3.6	5.8	3,05	6,4	3,2	6,5	3,2	4,5	2,45	2,8	3,5	3,9
1,75	3.1	7,5	3,9	6,8	3,25	7,3	3,5	7,3	3,3	5,0	2,55	3,2	3,7	4,25
2.0	3,25	8,6	4,25	7,55	3,55	8,15	3,8	8,1	3,5	5,5	2,75	3,6	3,9	4,6
2.5	3.8	10,6	4,9	8,85	4,25	9,65	4,45	9,6	3,8	6,45	3,0	4,35	4,3	5,2
3.0	4.4	12.4	5,6	10,0	4,95	11,0	5,2	11,0	4,2	7,4	3,35	5,1	4,7	6,0
3.5	5,1	14,3	6.35	11.2	5,7	12,4	5,9	12,3	4,65	8,4	3,7	5,85	5,15	6,6
4,0	6,05	16.2	7,1	12,3	6,45	13,8	6, 65	13,4	5,1	9,3	4,1	6,6	5,5	7,3
4,5	7.0	17,8	7,85	12,8	7,2	15,0	7,45	14,7	5,6	10,6	4,5	7,2	5,8	8,0
5.0	7,95	19,2	8,6	14,2	7,9	16,2	8,2	15,9	6,1	11.0	4,85	7,9	6.05	8,6
5,5	8.9	20,4	9,3	15,2	8,6	17,4	9,0	17,0	6,7	11,8	5,25	8,5	6,3	9,3
6,0	10.0	21,4	10,1	16,0	9,35	18,6	9,85	18,2	7,4	12,5	5,7	9.05	6,6	9,9
6.5	11,0	22,5	10,8	16,8	10,0	19,9	10,8	19,4	8,2	13,3	6,1	9,5	6,8	10,6
7.0	12,1	23,4	11,6	17,6	10,8	21,2	11,6	20,5	9,2	14,1	6,45	10,0	7,1	11,3
7,5	13,2	24,3	12,4	18,4	11,4	22,4	12,5	21,7	10,3	14,8	6,85	10,6	7,35	12,0
8,0	14,3	25,2	13,2	19,0	12,2	23,6	13,5	22,8	11,8	15,5	7,3	11,0	7,6	12,7
8,5	15.4	26,0	13.9	19.8	13,1	24,8	14,4	23,8						
9.0	16.4	26,8	14,8	20,4	13,9	26,0	15,4	24,9						
9.5	—	—	15,6	21,0	14,8	27,3								
10.0	—	—	16.4	21,5	15,8	28,5								

the Fermi surface at a concentration equal to N_{val}, S_F—total area of the Fermi surface, S_F^0—total area of the free-electron sphere at a concentration equal to N_{val}, ν_{ep}—electron-phonon collision frequency, ν_{ep}^{cl}—classical electron-phonon collision frequency, ν_{ed}—frequency of the collisions of the electrons with the impurities and defects, l—electron means free path, δ—skin-layer depth, E_F^0—Fermi energy of free electrons at concentration N_{val}, and ΔN and $\Delta\nu$ are the absolute errors in the determination of N and ν. At the end of the table are given the mean values of T_c for the samples used in the optical measurements.

The calculation of all the characteristics, with the exception of N and ν, was by means of the formulas given in[13], in which a single Fermi surface is assumed for all the valence electrons of the alloy.

DISCUSSION

1. It is seen from Table II that for the Nb-Sn alloys we have $N \ll N_{val}$, $v_F \ll v_F^0$, and $S_F \ll S_F^0$. This is due to the presence of a small number of Bragg planes intersecting the free-electron sphere in these alloys. The conduction-electron concentration of the Nb-Sn alloys is much lower than the corresponding values for pure Nb ($N = 4.49 \times 10^{22}$ cm^{-3})[14] and Sn ($N = 4.8 \times 10^{22}$ cm^{-3})[15]. This value is close to N for the V-Ga alloy[1-3].

It is seen from Table II that both the conduction-electron concentration N and the valence-electron concentration N_{val} decrease with increasing Sn content in the alloy. When the Sn content changes from 6 to 40%, the value of N decreases by a factor of 4 and N_{val} decreases 10%.

2. On the average, the value of ν in the investigated alloys is twice as large as in pure Nb ($\nu = 2.28 \times 10^{14}$ sec^{-1})[14] or Sn ($\nu = 2.26 \times 10^{14}$ sec^{-1})[15], and is approximately half as large as in the V-Ga alloy[3]. Yet the frequencies ν_{ep} are close to one another in all the cases under consideration. The indicated difference in ν is connected with the large value of ν_{ed} in the alloys, with ν_{ed} approximately 3—4 times larger in the V-Ga than in the Nb-Sn alloys. It should be noted that in the investigated alloys ν_{ed} amounts to only 25—30% of ν, which is much lower than in the V-Ga alloy[1-3]. In the latter, ν_{ed} reached 60% of ν.

It is seen from Table II that the dependence of ν on the composition has a minimum that corresponds to 34% Sn. At this same Sn concentration, a maximum is observed in the dependence of the mean free path l on the composition. These results may indicate that in sputtering a maximum amount of material of stoichiometric composition is produced at a small excess of Sn.

3. It is seen from Table II that in Nb-Sn alloys $l \ll \delta$, i.e., the skin effect, as expected, is normal.

Table II. Electronic characteristics of Nb-Sn alloys

Characteristic	Wt. % Sn						
	6	22	28	30	34	40	55
N, 10^{22} cm^{-3}	2.7	2,3	2,3	2,3	1,2	0,70	1,1
ΔN, 10^{22} cm^{-3}	0,15	0,2	0,3	0,3	0,1	0,1	0,3
N_a, 10^{22} cm^{-3}	5,3	5,5	5,4	5,4	5,3	5,3	5,2
N_{val}, 10^{22} cm^{-3}	26,4	26,3	25,8	25,6	25,2	24,5	23,7
v_F, 10^8 cm·sec^{-1}	0,74	0,67	0,68	0,68	0,49	0,38	0,48
v_F^0, 10^8 cm·sec^{-1}	2,30	2,29	2,28	2,27	2,26	2,24	2,22
S_F, 10^{-37} g^2·cm^2·sec^{-2}	1,8	1,6	1,6	1,6	1,2	0,9	1,1
S_F^0, 10^{-37} g^2·cm^2·sec^{-2}	5,5	5,5	5,4	5,4	5,3	5,2	5,1
ν, 10^{14} sec^{-1}	3,6	5,1	4,3	3,9	2,9	4,9	7,2
$\Delta\nu$, 10^{14} sec^{-1}	0,2	0,5	0,6	0,5	0,2	0,8	2,2
ν_{ep}, 10^{14} sec^{-1}	2,5	3,6	2,7	2,2	2,0	4,3	6,5
ν_{ep}^{cl}, 10^{14} sec^{-1}	0,5	1,4	1,9	2,1	1,4	1,1	2,3
ν_{ed}, 10^{14} sec^{-1}	1,1	1,5	1,6	1,7	0,9	0,6	0,7
l, 10^{-6} cm	0,20	0,13	0,16	0,18	0,17	0,08	0,07
δ, 10^{-6} cm (for $\lambda = 6\mu$)	4,5	6,0	5,2	5,3	7,7	11	9,7
E_F^0, eV	15,0	15,0	14,8	14,7	14,6	14,3	14,0
T_c, °K	7,2	16,1	17,2	16,8	17,2	17,65	10,2

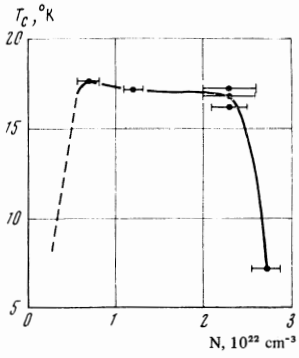

FIG. 4. Correlation between T_c and N for Nb-Sn alloys.

The presented data allow us to estimate the dimension of the crystallites: $L \sim v_F/\nu_{ed}$. The value of L in the investigated alloys turned out to be on the order of 40–70 Å. Thus, $l < L \ll \delta$. This inequality indicates that, on the one hand, the dimensions of the crystallites are sufficiently large so as not to limit the mean free path, and on the other hand the value of the skin layer is so large that the optical data pertain to thicknesses containing a very large number of crystallites. The latter circumstance means that there is sufficiently good averaging over the volume, i.e., that there is no influence of local inhomogeneities on the optical data.

4. A correlation (see Fig. 4), analogous to that observed for the V-Ga alloy[1-4], is observed between N and T_c for the Nb-Sn alloys. The $T_c(N)$ dependence is not monotonic but passes through a maximum. The maximum value of T_c is reached at $N \approx 0.7 \times 10^{22}$ cm^{-3}. For V-Ga, the maximum value of T_c occurred at $N = 2.2 \times 10^{22}$ cm^{-3} [1-4].

It should be noted that the character of the $T_c(N)$ dependence is the same for both systems of alloys. A sharp increase of T_c is observed for small N and a relatively smooth decrease is observed after the maximum for large N. The maximum value of T_c is higher for the Nb-Sn alloys and is reached at lower values of N.

It is seen from Table II that the correlation of T_c with S_F and with v_F has the same character for the Nb-Sn alloys as for the V-Ga alloys[1-3]. No correlation was observed between T_c and ν_{ep}; this may be due to the large error with which ν_{ep} is determined (20–30%).

5. If it is assumed that the weak-coupling approximation is applicable to the investigated alloys, then, by using the connection between N, N_{val}, and V_g given in[13] (formula (2.12) with allowance for (2.13)), or by using the sum rule[16] (formula (22)), we obtain an expression for the average modulus of the Fourier component of the pseudopotential $\overline{V}_g$:

$$|\overline{V}_g| = \frac{6\pi\hbar^3}{m}(N_{val} - N) \Big/ \sum_g n_g p_g = \frac{4}{\pi} E_F^0 \left(1 - \frac{N}{N_{val}}\right) \Big/ \sum_g n_g \frac{p_g}{p_F^0}. \quad (1)$$

Here $\hbar$ is Planck's constant, m the mass of the free electron, p_F^0 the Fermi momentum of the free electrons at a concentration N_{val}, p_g the distance from the center of the Γ band to the Bragg plane with index g, n_g the number of physically equivalent Bragg planes with index g, and the summation is over the systems of physically-nonequivalent Bragg planes intersecting the free-electron sphere.

Using the values of N and N_{val} given in Table II, and the values of n_g and p_g/p_F^0 for the A-15 structure from[1,2,13], we found that $|\overline{V}_g|/E_F^0 = 0.015$–$0.016$ for the investigated alloys. To check on this result, it is necessary to measure the optical properties of the Nb-Sn alloys in the short-wave region of the spectrum, so as to determine V_g by an independent method.

The value of $|\overline{V}_g|/E_F^0$ for an alloy containing 33% Ga and 67% V, calculated from formula (1), is 0.015. Direct measurements in the short-wave region of the spectrum yield for this alloy[3]

$$\frac{|\overline{V}_g|}{E_F^0} = \sum_g n_g \frac{p_g}{p_F^0} \frac{|V_{eg}|}{E_F^0} \Big/ \sum_g n_g \frac{p_g}{p_F^0} = 0.018.$$

We see that the two values for the V-Ga alloy are close to each other as well as to the value obtained for the Nb-Sn alloys.

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