STUDY OF THE SUPERCONDUCTING PROPERTIES AND THE STRUCTURE OF TIN FILMS OBTAINED BY REACTIVE SPUTTERING

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Submitted August 15, 1969

Zh. Eksp. Teor. Fiz. 58, 528–534 (February, 1970)

The critical temperature T_c, transverse critical magnetic fields $H_c^\perp$ and resistivities of microcrystalline tin films, obtained by reactive cathode sputtering, are measured. The relation between T_c and $H_c^\perp$ and the film structure as studied with an electron microscope is investigated. It is found that increase of T_c and $H_c^\perp$ correlates with a decrease in the grain size. The electron mean free path l is determined from resistance and magnetic measurements. The dependence of $H_c^\perp$ on l is compared with the theoretical calculation.

IT is known that a decrease in the thickness of superconducting layers leads (beginning with certain thicknesses) to an increase in the critical temperature of the sample. Cohen and Abeles[1] observed a similar behavior of aluminum samples following a decrease in the dimensions of the grains making up the film, while the thickness of the layers was almost unchanged. In [1], the aluminum films were prepared by the reactive sputtering method, which makes it possible to obtain samples with different grain dimensions. However, the formation of an oxide layer over the grain boundaries was very probable. Since Rühl[2] has shown that the oxidation of the aluminum layers leads to a rise in the critical temperature of the samples, the result obtained in [1] can be connected not only with a pure size effect, but also with oxidation.

To clarify the problem of the degree to which the increase in the critical temperature with decrease in crystal size has a general character, and is not connected with the oxidation effect, it is of interest to carry out measurements in films of a metal whose oxidation leads to a decrease in T. According to Rühl,[2] such a superconductor is tin, which has also been chosen as an object of study in our research.

We measured the critical temperature T_c, the transverse critical magnetic field $H_c^\perp$, and the resistivity ρ and investigated the dependence of these quantities on the average grain size in the film.

The film samples of tin were prepared by the cathode sputtering method with an ion point sputterer (IPS) apparatus.[3,4] Cathode sputtering was carried out under conditions of broad beam and low pressure. The gaseous medium was spectrally pure krypton or a mixture of krypton and air. The residual gas pressure in the apparatus amounted to $\sim 10^{-7}$ mm–5×10^{-5} mm Hg. The total gas pressure of the mixture was constant for all experiments–5×10^{-5} mm Hg. The partial pressure of air changed from experiment to experiment–from 0 to 5×10^{-5} mm Hg. The accelerating voltage was 3.75 kV. The gas discharge current was 750 mA. The sputtering rate depended slightly on the air concentration in the gas mixture and amounted to about 19 Å/min. The cathode material was tin with a ratio R(293°K)/R(4.2°K) = 10 000. The backing material was of two types. For film samples intended for the study of the superconducting properties, flat polished glass backings were used, with four platinum leads. For samples intended for the study of the structure in an electron microscope, water-polished NaCl crystals were employed. To obtain tin films with sharp edges, masks of phosphor bronze were used with a thickness of 40 μ. The temperature of the backing in the sputtering was ~80°K.

The table shows the basic characteristics of the prepared film samples. The air concentration in the krypton-air mixtures was determined on the basis of known relations.[5] The mean grain size in the film was determined by methods used in metallography.[6] The thickness of the film samples was determined by means of an M114 microinterferometer and varied from 650 to 2000 Å. In this range of thicknesses, no appreciable change of T_c with sample thickness was observed for the tin samples (see Fig. 3 below).

The sample structure was studied by transmission in the electron microscope Tesla VS-513 at an accelerating voltage of 80 kV. The resolution of the electron microscope was ~5 Å, the magnification of the electron microphotograph, × 250 000. Figure 1 shows electron

Basic Characteristics of Tin Film Samples

No. of sample	Air concentration, %	Mean grain dimension a, Å	Thickness,* Å	$\frac{R\,(293°K)}{R_{res}}$	T_c, °K	$\lvert dH_c^\perp/dT\rvert_{T_c}$, kOe/deg
1	0	450	1400	—	3.85	—
2	2	410	1560	—	3.76	—
3	3	—	950	4.3	3.89	—
4	9	600	1500	3.0	3.84	0.33
5	10	—	1900	1.72	4.29	—
6	15	460	2000	3.3	4.06 **	0.47
7	21	250	1900	1.87	4.13	—
8	34	220	1110	1.43	4.28	1.33
9	39	180	1100	1.62		
10	40	200	950	1.21	4.51	2.65
11	42	180	—	1.27	—	—
12	46	100	900	1.17	4.52	2.85
13	51	100	—	1.13	4.57	2.82
14	55	100	650	1.14	4.66	3.04
15	82 ***	50	1400	—	—	—
16	100 ***	10	4600	—	—	—

*Thickness of film samples studied in an electron microscope was smaller by a factor of five.

**For this sample, a departure of the dependence $H_c^\perp(T)$ from a straight line was observed; therefore, in the calculation of $\lvert dH_c/dt\rvert_{t=1} \equiv \lvert dH_c^\perp/dT\rvert_{T_c} T_c$ (see Fig. 5), we used the value $T_c = 3.76$, which was obtained by extrapolation of the straight segment to H = 0.

***The characteristics of the samples changed appreciably with time.

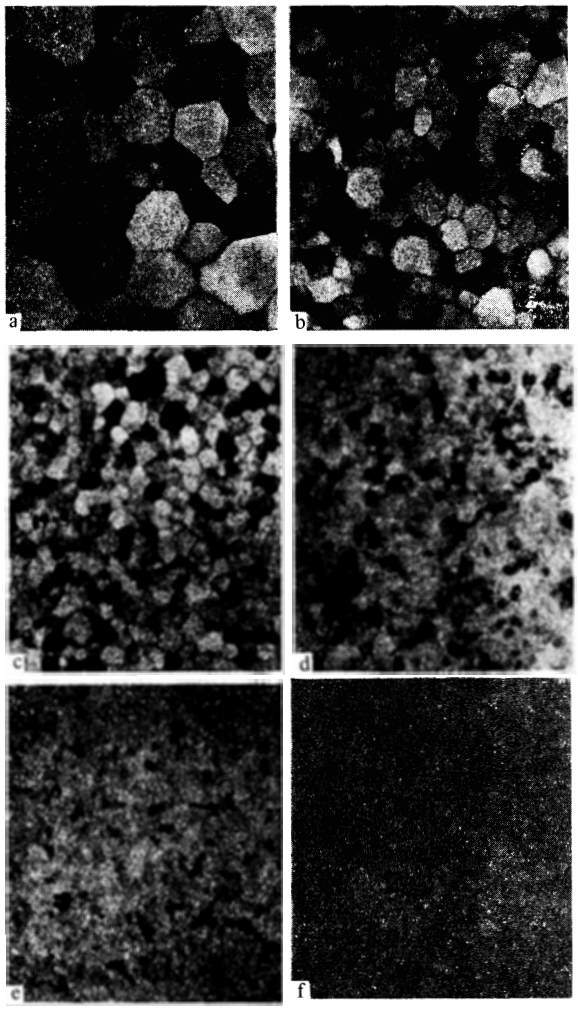

FIG. 1. Structure of tin film samples, prepared by cathode sputtering, for different air concentration c in a mixture of krypton and air. The electron microphotographs were obtained by transmission, X250,000: a – c = 0, mean grain size a = 450 Å; b – c = 21%, a = 250 Å; c – c = 39%, a = 180 Å; d – c = 46%, a = 100 Å; e – c = 82%, a = 50 Å; f – c = 100%, a = 10 Å.

microphotographs of six tin samples having different grain sizes.

With increase in the air concentration from 0 to 100%, the grain size in the krypton-air mixture decreased from 450 to ~10 Å. The individual gains are not seen in Fig. 1e. With account of the resolution of the electron microscope (5–10 Å), one could estimate the upper limit of the grain size at ~10 Å. Electronographic investigation of the given sample gave an estimate ~10 Å (from the half-width of the diffraction ring of the electronogram).

Curves of the superconducting transition were taken at continuous temperature variation for various fixed transverse magnetic fields. The magnetic fields were generated by a superconducting solenoid, calibrated by a Hall pickup. The measurement current through the sample amounted to 50 μA; the transition curves were not shifted following a change in current to 200 μA. The measurements were carried out at temperatures below 4.2°K. The temperature was determined both from the

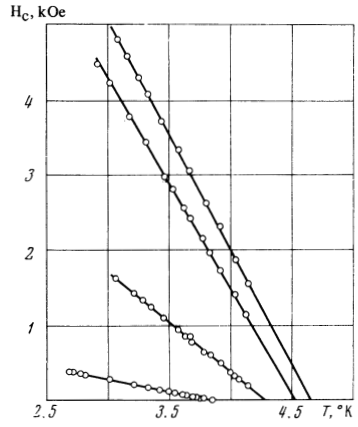

FIG. 2. Dependence of the critical magnetic fields on the temperature for samples Nos. 4, 8, 12, 14 (in order of increasing T_c).

helium vapor pressure in the cryostat and by means of an Allen-Bradley carbon thermometer. For films with $T_c < 4.2°K$, the critical temperature was determined from the transition curves in zero magnetic field. After T_c, the temperature for which the sample resistance $T = {}^1/_2 R$ was taken, where R_n is the resistance of the sample in the normal state. The critical temperature of samples with $T_c > 4.2°K$ was determined by extrapolation of the $H_c^{\perp}(T)$ dependence to H = 0. The set of curves $H_c^{\perp}(T)$ for several samples is shown in Fig. 2. The temperature corresponding to the experimental points on this graph was determined from the average of the transition in a constant field.

The dependence of the critical temperature on the mean grain size obtained for our samples is shown in Fig. 3. Figure 4 gives the dependence of the derivative of the critical magnetic field with respect to the temperature $|dH_c^{\perp}/dT|_{T_c}$ on the average grain size.

The experiments we carried out show that as the relative amount of air in the sputtering increased, beginning with a certain value, some dependence is observed of the physical characteristics of the samples on the time. Therefore, we give data only for samples obtained by sputtering at certain air concentrations. In this case, the time dependence is seen to be weak and can be neglected.

The dependence that we obtained of the critical temperature on the mean grain size for tin films indicates the general character of the effect observed in [1], to

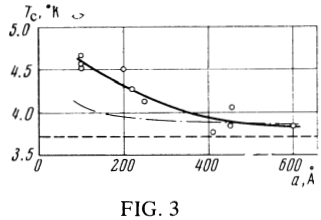

FIG. 3

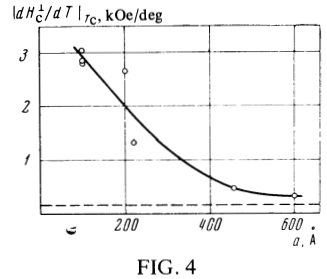

FIG. 4

FIG. 3. Dependence of the critical temperature on the mean grain size. The dashed curve corresponds to the critical temperature of pure massive tin; the dot-dash line shows the dependence of T_c on the thickness of the tin films (from the data of [7]).

FIG. 4. Dependence of the derivative $|dH_c^{\perp}/dT|_{T_c}$ on the mean grain size. The dashed curve shows the value for pure massive tin.

wit: the critical temperature increases with decrease in grain size. Evidently the assumption that the role of oxygen in samples prepared by the reactive method consists in the stabilization of the fine crystalline structure is valid in our case also.

It is interesting to note that the maximum critical temperature obtained in our experiments is identical with the T_c of tin films freshly condensed at the temperature of liquid helium. The corresponding grain sizes in the two cases are very close in magnitude (100 Å in the given case and 90 Å in the freshly condensed samples[8]).

For films with grain size 600 Å and smaller, the mean free path of the electrons l_R (the R means that l is computed from the resistance) does not exceed 200 Å. The estimate of l_R was obtained from the formula $l_R = l_{R0}(r-1)$ where l_{R0} applies to pure metal at room temperatures and $r = R(293°K)/R_{res}$.[1)] We used the value $l_{R0} = 95$ Å. According to what was said above, the condition $l \ll \xi_0$ is satisfied for the films considered, since the coherence length for tin is $\xi_0 = 2300$ Å.[9] In this case, the Ginzburg–Landau parameter is given by the expression $\kappa = 0.75\,\lambda_L(0)/l$ and for the films mentioned above it is always greater than $1/\sqrt{2}$. Consequently, we can consider our sample as type II superconductors, and $H_c^{\perp}$ of the film should be identical with the upper critical field $H_{c2} = \Phi_0/2\pi\xi_T^2$, where ξ_T is the temperature-dependent coherence length, Φ_0 = the flux quantum. Making use of the relation[2)]

$$\xi_T = 0.85\sqrt{\xi_0 l}(1-t)^{-1/2},$$

where $l \ll \xi_0$, $t = T/T_c$, we obtain

$$|dH_c^{\perp}/dt|_{t=1} = 4.53\cdot 10^{-8}(l\xi_0)^{-1}. \qquad (1)$$

Figure 5 gives a graph of the dependence of $|dH_c^{\perp}/dt|_{t=1}$ on $1/l_R$. For comparison, we have plotted on this same graph the points computed from the data of Harper and Tinkham.[10] They cluster well about our straight line. It is seen from Fig. 5 that up to $l_R = 20$ Å, a linear dependence of $|dH_c^{\perp}/dt|_{t=1}$ is observed, while the slope of the line is somewhat greater than would follow from (1) if we take $\xi_0 = 2300$ Å.[3)]

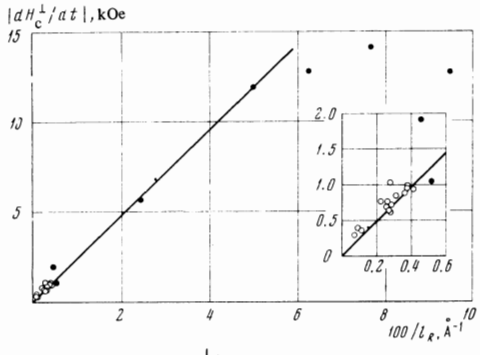

FIG. 5. Dependence of $|dH_c^{\perp}/dt|_{t=1}$ on the free path length l_R: ● – according to the measurements of the present research, ○ – according to the data of [10]

By giving the value $\xi_0 = 2300$ Å and using (1), we can compute the value of l_H (the index H means that these values were taken from magnetic measurements) which are found in reasonable agreement with the values of l_R.

The value of l is shown to be several-fold smaller than a. This can be connected either with the effect of electron scattering by defects existing inside the grains and observed by electron microphotographs in the form of dark spots of size 5–10 Å, or with the small transmission coefficient of electrons through the barriers which the grain boundaries represent.

We wish to call attention to the fact that from the data on the critical magnetic field of the films one can estimate the density of electron states by using the theoretical expressions for type-II superconductors at $l \ll \xi_0$. Unfortunately, such an estimate is difficult in our case, since more accurate measurements of the film thicknesses are necessary and furthermore, the problem of the applicability of the corresponding theoretical expressions for our samples is not completely clear.

Possible reasons for the observed rise in the critical temperature in fine crystalline films can be the change in the phonon spectrum in fine-grained material, the quantization of the motion of the electrons in separate crystals,[11] or the electron evaporation through the barrier.[12] However, there is no convincing experimental evidence to date in support of the mechanisms mentioned.

Explanation of the situation connected with the superconductivity in fine crystalline samples requires additional study, both theoretical and experimental.

In conclusion, the authors express their gratitude to B. N. Samoĭlov for interest in the research, and to B. E. Yavelov and R. O. Zaĭtsev for discussions.

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1) By R_{res} we mean the resistance measured immediately after the transition to the normal state.

2) The corresponding theory suggest scattering by point defects; however, there is a basis [1] for application of the expressions obtained in the case of scattering by grain boundaries.

3) If we assume that ξ_0 changes from sample to sample in correspondence with change in T_c ($\xi_0 = 0.18\,\hbar v_F/kT_c$; v_F here is assumed to be constant), then the slope of the line is equal to theoretical one for $\xi_0^{\infty} = 2300$ Å, where ξ_0^{∞} is the correlation parameter pertaining to a metal with $T_c = 3.72°K$.

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Translated by R. T. Beyer
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