# Correlation of $T_c$ with the resistance ratio and $Nb_3Ge$ film structure

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(Submitted 5 July 1979)
Pis'ma Zh. Eksp. Teor. Fiz. **30**, No. 9, 561–565 (5 November 1979)

Various correlations of the critical temperature $T_c$, resistance ratios and $Nb_3Ge$ film structures are investigated. A single-valued, $T_c$ relationship between films and bulk samples is shown. A method of cathode sputtering involving a composite target is used to attain total superconductivity at the record temperature of 22.5 K, $T_c = 22.7$ K, and $T_c^{(H)} = 23.4$ K.

PACS numbers: 74.10. + v, 73.60.Ka, 74.70.Lp

The study and structural development of high-temperature superconductors are the necessary conditions for elevating their critical temperatures $T_c$. The correlation of $T_c$ with the resistance ratio $\gamma = R_{300}/R_n$ (where $R_{300}$ and $R_n$ are resistances at 300 K and residual), reflects a tendency of $T_c$ to increase with improvement in the film quality.[1,2] We obtained additional results for $Nb_3Ge$, which indicate a more complex nature of the relationship between $T_c$, $\gamma$ and the film structure.

We observe a sharp correlation of $T_c$ and $\gamma$ (Fig. 1) which is similar to the correlation established in Ref. 2, for samples that satisfy two conditions: (1) samples are obtained with a sufficient amount of oxygen and (2) $\gamma$ values are not significantly

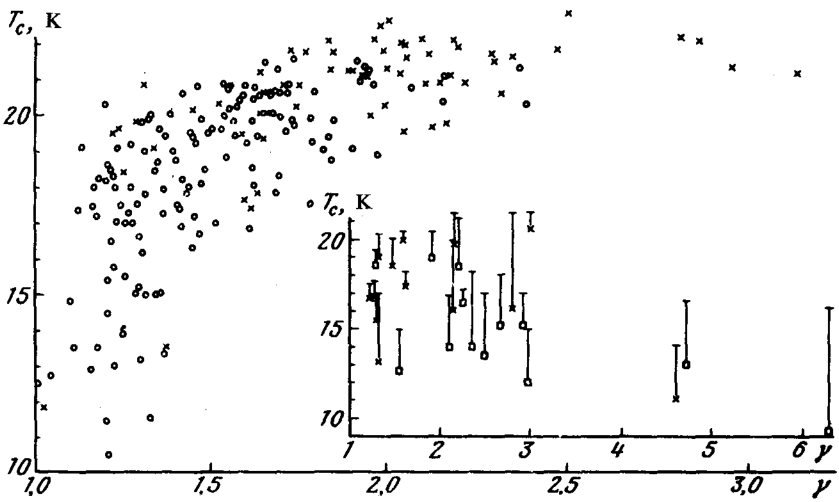


FIG. 1. Correlation of $T_c$ and the resistance ratio $\gamma$ for $Nb_3Ge$ films. $T_c$ values determined with respect to center of transition. Crosses denote samples with stoichiometric, and circles non-stoichiometric compositions. The insert shows $T_c$ and $\gamma$ for samples, obtained at oxygen deficit (crosses) and for films corresponding to σ-phase composition (squares). Upper ends of bars denote $T_c^{(H)}$.

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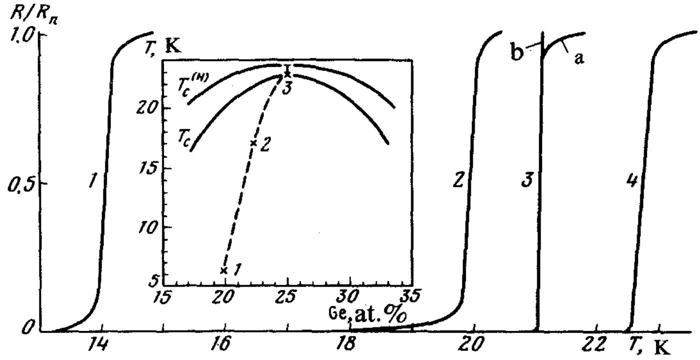


FIG. 2. Examples of transitions into the superconducting state for $Nb_3Ge$ films obtained under various conditions. Insert shows dependence of $T_c$ and $T_c^{(H)}$ on film composition (solid curves). Dashed line shows dependence of $T_c$ on $\beta$-phase composition.

affected by their $\alpha$- and $\sigma$-phases. A number of samples of a different composition were prepared in each experiment and the $\gamma$ maxima were observed which corresponded to the compositions of $\alpha$-, $\beta$- and $\sigma$-phases. To satisfy the second condition, samples corresponding to the $\beta$-phase were picked in the composition range between two $\gamma$ minima. Figure 1 shows a more physically-valid correlation of $T_c$ (but not of the onset of the $T_c^{(H)}$ transition as in Ref. 2) with $\gamma$. Unlike Ref. 2, but in line with Ref. 3, we identified samples with high $T_c$ ($\gtrsim 20$ K) at lower $\gamma$ ($\sim 1.3$). The maximum values of $T_c$ and $\gamma$ were attained for stoichiometric compositions.

Figure 2 shows examples of transitions of films with different $\gamma$ which were prepared in various regimes. The low precipitation rate of films (0.1–0.3 Å/sec) led to low $\gamma = 1.0$–$1.3$ and $T_c = 12$–$15$ K due to a large number of impurities (curve 1). For samples obtained in "hard" regimes [4] with sufficient oxygen, the presence of "tails" on the transition curves (curve 2) is characteristic, and electron microscopy reveals a well-defined grain structure (Fig. 3). These exhibit unusually high $T_c$ at $\gamma \sim 1.3$. The high-temperature phase of such films, isolated inside the grain, is protected by an amorphous oxide layer that is enriched with oxygen from the hexagonal ($Nb_5Ge_3O_x$) and the $\beta$-phase. In addition to this we believe their $T_c$ remain high because the interaction of energetic particles leads to the formation of, first of all, point defects that have a weak effect on $T_c$ while lowering $\gamma$.

Samples with high $\gamma$ and $T_c$ obtained in "soft" regimes [5] also have sharp transition curves (curves 3 and 4). The total transition width $\Delta T_c$ for films prepared at voltages $V \sim 1000$ V did not exceed 0.7 K (curve 3a), and when the working current increased, it was reduced to hundredths of a degree (curve 3b). Curve 4 refers to a sample with $\gamma = 2.5$ which was obtained under the optimal conditions, having $T_c = 22.7$ K, $T_c^{(H)} = 23.4$ K and being fully superconducting at 22.5 K.

Correlation for samples obtained at an oxygen deficit and corresponding to a dip in the value of $T_c$ as a function of composition [5] is shown in the insert in Fig. 1. Clearly, the nature of this correlation is opposite, i.e., a lack of phase stabilization in $Nb_3Ge$, especially in "hard" regimes leads to a considerable increase in $\gamma$ and a lowering of $T_c$.

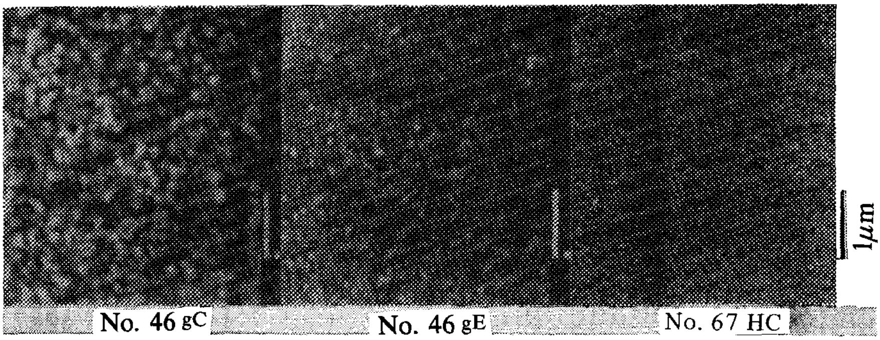


FIG. 3. Structural microphotographs of $Nb_3Ge$ films obtained in "hard" regimes ($V = 2$ kV). Sample No. $46^g$: $T_c = 19.2$ K, $T_c^{(H)} = 20.4$ K and thickness $\sim 1$ $\mu$m (superscripts "$C$" and "$E$" indicate "center" and "edge" of sample); sample No. $67^h$: $T_c = 16.5$ K, $T_c^{(H)} = 17$ K and thickness $\sim 0.4$ $\mu$m.

The same insert indicates $T_c$ and $\gamma$ of samples corresponding to the $\sigma$-phase composition. Anti-correlation is also observed for these samples. Even high $T_c$ values are attained for such compositions. Low values of $\gamma$ point to inhomogeneity of such films, and high $T_c$, an absence of a high-temperature phase. Conversely, high $\gamma$ values for these indicate the formation of practically one $\sigma$-phase, which sharply lowers $T_c$.

The dependence of $T_c$ and $T_c^{(H)}$ on sample composition for a better series are shown in the insert in Fig. 2. There also a dashed line shows a well-defined dependence of $T_c$ on the composition of the strictly $\beta$-phase, which connects three points. Point 1 corresponds to a stable $\beta$ phase that is formed by conventional metallurgical means. Point 2 refers to an unstable $\beta$ phase obtained by rapid tempering,[6] point 3 to a metastable $\beta$-phase of stoichiometric composition obtained in the films. The weak dependence of $T_c$ on film composition (as also anti-correlation of $T_c$ with $\gamma$, is shown in the insert in Fig. 1) attests to the existence in the non-stoichiometric samples of considerable amounts of the $\beta$ phase with a near-stoichiometric composition. This confirms the fact that there exist stabilizing factors that take part in the process of film formation and which made this phase competitive with respect to growth of both the $\alpha$- and $\sigma$-phases. The stabilization is determined by the penetration of oxygen into the lattice when the film is formed, and its precipitation onto the phase boundaries (and into the $\sigma$ phase) and "freezing" of the metastable $\beta$ phase after the withdrawal of oxyen when the optimized temperature of substrate $T_d$ is picked.[5] According to this model both the $\alpha$-phase and $Nb_3Ge$ phase should form under optimal conditions in samples with non-stoichiometric composition. However, in the absence of stabilization $\beta$-phase composition in the series will be close to $Nb_4Ge$ with $T_c \sim 6$ K. Films containing $\sim 20$ at.% Ge will then contain a single A-15 phase and exhibits anomalously high $\gamma$ and low $T_c$. The sample closest to this case was one we obtained in a "hard" regime with an acute oxygen deficiency for which $\gamma = 4.6$ and $T_c \approx 11$ K. For a less acute oxygen deficit the $\gamma$ maximum is displaced in the direction of stoichiometric composition, the value of $\gamma$ decreases, and $T_c$ increases. The exact position of the $\gamma$ maximum with respect to film composition in the series shows a $\beta$-phase composition which is stabilizing under the preparation conditions of a given series. In the case of small oxygen deficit the value of $\gamma$ was normally lower than at its optimal quantity since a $\beta$ phase with a certain composition spread is formed in the samples due to fluctuations. Their transitions are broadened to 2 K and up. Excessive amounts of oxygen reduce $\gamma$ and, consequently, also $T_c$ since a considerable portion of oxygen remains in the $\beta$ phase, broadening its lattice and acting as a harmful impurity.

The observed correlation of $\gamma$ with $\Delta T_c$ is associated with the phase composition. The value of $\gamma$ for various phases also correlate with $T_d$. A small overshoot of the optimal $T_d$ has led to an increase in $\gamma$ of samples with the $\sigma$ phase, and a lowering of $T_d$ improved the growth of the $\alpha$ phase.

It is interesting to note that films with high values of $T_c$ may be obtained with perfect specular surfaces as also with grey or even dark shades. With increasing regime "hardness" film thickness, the relative area of Ge at the target, number of cycles with a single target, the films grew darker. The single-valued relationship of color and $\gamma$ and grain size was not observed (from among the photographs in Fig. 3, No. 46 [3E] is the brightest film). The shade of dark samples in the series varied with composition; moreover, the $T_c$ maximum was attained near the edge of darkening and the highest specularity, at Nb-rich compositions. A relationship between shade and the pillar-like growth of films [7] may be assumed as the result of precipitation of Ge, formation of oxides and the $Nb_5Ge_3O_x$ phase on the surface.

The results obtained show that the resistance ratios yield comprehensive information on the structure of superconducting films, which permits one to have insight into the nature of high-temperature superconductivity.


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