The role of oxygen in the formation of the Nb_3Ge film structure with high critical temperatures

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We show that in order to form superconducting Nb_3Ge films with record high T_c, oxygen, which stabilizes the A-15 lattice at the film boundary and facilitates the occurence of seeds of the high-temperature phase, must be present. Total superconductivity was attained at 22.2 °K, the critical temperature at $T_c = 22.5$ °K and the onset of superconducting transition at 23.2 °K.

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Many facts point to the inherent instability of high-temperature superconductors.[1-4] In order to exceed the current record values of critical temperatures T_c stabilization mechanisms of their high-temperature phases must be investigated. Most interesting from this viewpoint is the compound Nb_3Ge, the only material today which is fully superconducting at the boiling temperature of hydrogen. A number of recent works note the positive role of oxygen in the formation of Nb_3Ge with a high T_c.[5,6] This work is dedicated to the investigation of the stabilizing role of oxygen in the process of formation of Nb_3Ge films with high, and record, critical temperatures.

Experiment. Nb_3Ge films were prepared by a d.c. cathode sputtering method using a composite target.[7] Sputtering was carried out in an argon atmosphere with various oxygen (and nitrogen) concentrations. From 10 to 13 specimen with different composition were prepared simultaneously.

Sputtering conditions were varied between the following limits: voltage $V = 480$–2300 V, argon pressure $P = 0.2$–1 tor. A four-probe method was used to measure film transition into the superconducting state. Temperature was determined with accuracy better than 0.1 K. Liquid hydrogen was used for control purposes. A number of films were subjected to x-ray microanalysis of composition and impurities. Auger spectroscopy was used to study the distribution of components and impurities in the bulk and on the film surface.

Results. The effect of oxygen on T_c of Nb_3Ge films was investigated over the entire interval of P and V (at powers $\lesssim 3$ W/cm^2, limited by Ge melting). High-T_c films were obtained in "hard" ($P = 0.2$–0.4 tor, $V \gtrsim 1700$ V) and "soft" ($P = 0.5$–1 tor, $V \lesssim 1700$ V) sputtering regimes (target-to-substrate distance 2 cm). Inspite of a certain arbitrariness, such a division is associated with real differences in the specimen properties.

In the "hard" mode, specimen with $T_c \sim 20$ K were only obtained in argon which contained $5 \times 10^{-4}\%$ oxygen, for instance in spectrally-pure argon (99.995%, $2 \times 10^{-3}\%$ nitrogen). In 99.999% pure argon (the principal impurity is nitrogen) or in spectrally-pure argon scrubbed for oxygen to $2 \times 10^{-5}\%$, T_c was down to 10–15

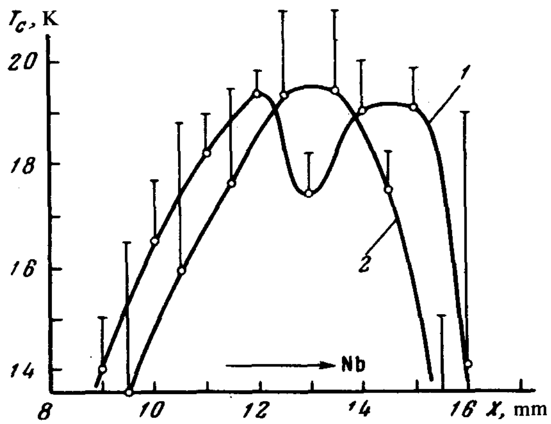

FIG. 1. Dependence of T_c of Nb_3Ge films on position on the substrate. This position characterizes specimen composition ($V = 2000$ V, $P = 0.3$ tor). Curve 1—for oxygen pressure 2×10^{-6} tor; curve 2—10^{-5} tor. Onset of transition into superconducting state shown for each point.

K. High-temperature highly-reproducible films were formed at increased partial oxygen pressures in the setup to $(0.4–3.0)\times10^{-5}$ tor. Experiments involving different O_2 content in argon have clearly established the stabilizing role of oxygen in the formation of Nb_3Ge films under the influence of various destructive factors: exposure to energetic particles ("hardness" of the regime), nitrogen admixture, deviation of substrate temperature T_D from optimal, etc.

High-T_c films obtained in "hard" regimes, are characterized by the following: a resistance ratio at 300 K and 25 K $R_{300}/R_{25} \approx 1.2–1.6$, presence of "tails" on the transition curves and increased seed size with higher O_2 content in argon. Two maxima were obtained in the dependence of T_c on composition (Fig. 1) in the case of sputtering in argon with a certain oxygen deficit ($(1–2)\times10^{-6}$ tor). Moreover, the stoichiometric composition corresponded to a local minimum T_c and an anomalously-high ratio R_{300}/R_{25} which attained 4.6.

Films obtained in "soft" regimes were characterized by $R_{300}/R_{25} = 1.6–3.0$, well-defined transition curves and a single maximum in the dependence of T_c on composition. The critical thickness was $\frac{1}{3}-\frac{1}{4}$ the normal size, becoming smaller as the regime became "softer" (even at a thickness of 800 Å $T_c^{(H)} = 19$ K). Formation of high-T_c films required $2\times10^{-5}\% O_2$ in argon over the entire broad range of P and V. The critical temperature increased with improved conditions for purity and moderation of regimes. The maximum purity was attained at $V = 550–700$ V and $P = 0.65–0.8$ tor. At oxygen pressures in the setup of $(0.2–1.0)\times10^{-6}$ tor in an interval of the highest purity ($V/P \sim 1$ kV/tor) a region was discovered where samples similar to those obtained in "hard" regimes with oxygen deficit were formed (Fig. 2). In this region oxygen enrichment helped increase the T_c of specimen. Films with maximum T_c were obtained at the boundary of the maximum purity region with "softer" regimes. Total superconductivity was attained at 22.2 K with $T_c = 22.5$ K and $T_c^{(H)} = 23.2$ K. Significant dependence of T_c on the film deposition rate was not observed. Specimens with $T_c > 21$ K were obtained in the rate interval 0.5–6 Å/sec. The optical $T_D = 825 \pm 20$ °C. The oxygen content in the films was $\lesssim 2\%$ (less in "soft" regimes), and nitrogen and other impurities $< 1\%$ (even at $2\times10^{-3}\%$ nitrogen in argon). The

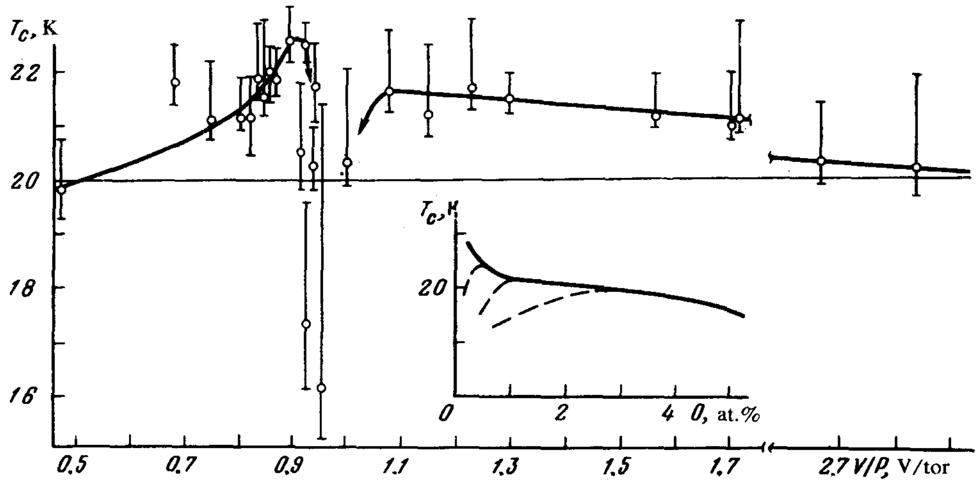

FIG. 2. Dependence of T_c on V/P for "soft" regimes. Partial oxygen pressure outside the chamber—(0.2–1)$\times 10^{-6}$ tor. Breaks indicate onset and end of transition. The dependence of T_c on oxygen content in films is shown qualitatively in the inset. Dotted lines show effect of disruptive factors.

oxygen content at the surface ~1 atom per cell, with the thickness of the oxygen-rich layer increasing with enhancement of regime "hardness" and film thickness.

Discussion. A more stable σ-phase interferes with the formation of the A-15 phase in Nb_3Ge films near stoichiometry.[8] Having penetrated the lattice, oxygen increases its constant, reduces tetragonal stress and stabilizes it although reducing T_c. It is important to stabilize both the A-15 phase seeds in the early layers of precipitated film[9] and its surface (protecting it at the same time from energetic particles).

The presence of oxygen at a depth in a film with A-15 lattice is unfavorable energy-wise; oxygen is forced out at the grain boundary and onto the surface (this resembles zone cleaning), i.e., oxygen here basically plays the role of a catalyst. In the process of film growth the Nb and Ge atoms "open up:" in the oxygen-rich surface layer lattice formation also occurs in the lower part of this layer. Both oxygen deficit (absence of stabilization) and an excess of it (partial entrapment inside a film) lower the T_c (inset in Fig. 2).

The substrate temperature should guarantee a reasonable atomic diffusion rate but hinder the intensive growth of the σ-phase (experiment yields 650 C $\lesssim T_D \lesssim$ 900 °C). The model also explains other results. The destabilizing factors require an increased quantity of oxygen to achieve high T_c; this leads to distended transitions for which the thickness of an "oxide" layer on the grains exceeds the coherence length. An increase in the oxygen content of films with a substantial O_2 deficit in argon was observed. The lowering of the coefficient of attachment of oxygen to a film growing under optimal conditions, is associated with the presence of a thin surface layer heavily enriched with oxygen. Sorption of oxygen increases under the conditions of its deficit due to defective lattice structure.

A stabilizing role is also played by some deviation of composition from stoichiometric (Fig. 1). For a fixed stoichiometry and oxygen insufficiency a sharp increase in the number of antistructural defects disturbs the intactness of chains as it lowers T_c. The averaged Heller radii of elements that are in nonequivalent A-15 lattice points, converge somewhat and a stability is attained that preserves the type of lattice while the ratio R_{300}/R_{25} increases sharply.

Conclusion. Oxygen, evidently, is not the unique admixture that is capable of stabilizing the A-15 lattice.[6,10] The effectiveness of oxygen in increasing the T_c is associated with its displacement to the film surface. The stabilizing effect of admixtures may be used to produce new superconducting compounds. The critical temperature may also be increased in Nb_3Ge provided purity with respect to oxygen is improved and, concurrently, destabilizing effects are minimized.

[1]B.T. Matthias, Physica **69**, 54 (1973).

[2]L.R. Testardi, Phys. Rev. **B5**, 4342 (1972).

[3]Yu.A. Izyumov and E.Z. Kurmaev, Usp. Fiz. Nauk **113**, 193 (1974); [Sov. Phys. Usp. **17**, 356 (1974)].

[4]A.I. Golovashkin and T.I. Kuznetsova, Preprint FIAN, No. 29, No. 156, 1978.

[5]J.R. Gavaler, J.W. Miller and B.R. Appleton, Appl. Phys. Lett. **28**, 237 (1976); R.A. Sigsbee, IEEE Trans. on Magn., V. Mag. **13**, 307 (1977); R.E. Somekh, Proc. LT-15 **1**, 398 (1978).

[6]A.B. Hullak, R.H. Hammond, T.H. Geballe and R.B. Zubeck, IEEE Trans. on Magn., v. Mag. **13**, 311 (1977).

[7]A.I. Golovashkin and E.V. Pechen', Fiz. Tverd. Tela **21**, No. 4 (1979); [Sov. Phys. Solid State 21, No. 4 (1979)]. Materialy NT-20, part 3, 181 (1978).

[8]D. Dew-Hughes, Preprint Brookhaven Lab., 1975.

[9]J.R. Gaveler, M. Ashkin, A.I. Braginsky and A.I. Santhanam, Proc. LT-15 **1**, 400 (1978).

[10]R.E. Enstrom, J.J. Hanak, J.R. Appert and K. Strater, J. Electrochem. Soc. **119**, 743 (1972).