Superconductivity of nonstoichiometric niobium carbide

Yu. S. Karimov and T. G. Utkina
Institute of Structural Macrokinetics, Academy of Sciences of the USSR

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Heat treatment of niobium carbide alters the state of its carbon sublattice and causes a significant change in the superconducting transition temperature. The electron pairing in this case might be due to an interaction of the conduction electrons with the local modes of tunneling configurations which arise upon a local restructuring of a small group of carbon atoms.

Niobium carbide, NbC_x, is a classical interstitial compound with a homogeneity region $0.72 < x < 0.99$ (Ref. 1). The niobium atoms form an fcc lattice whose octahedral interstitial positions are occupied by carbon atoms. A certain fraction $(1 - x)$ of the interstitial positions remains vacant. The niobium sublattice forms a rigid framework, which is destroyed only when the carbide melts ($T_m \sim 3308$–3886 K). The carbon atoms, in contrast, move comparatively freely among octahedral interstitial positions. In particular, an ordering of the carbon sublattice is observed at ~ 1300 K for compositions near Nb_6C_5 (Ref. 2).

Niobium carbide is a superconductor. Its highest superconducting transition temperature, $T_c = 11$ K, is exhibited by the carbide near the stoichiometric composition, NbC. As the carbon concentration is reduced, T_c falls sharply ($T_c < 2$ K for $NbC_{0.82}$;

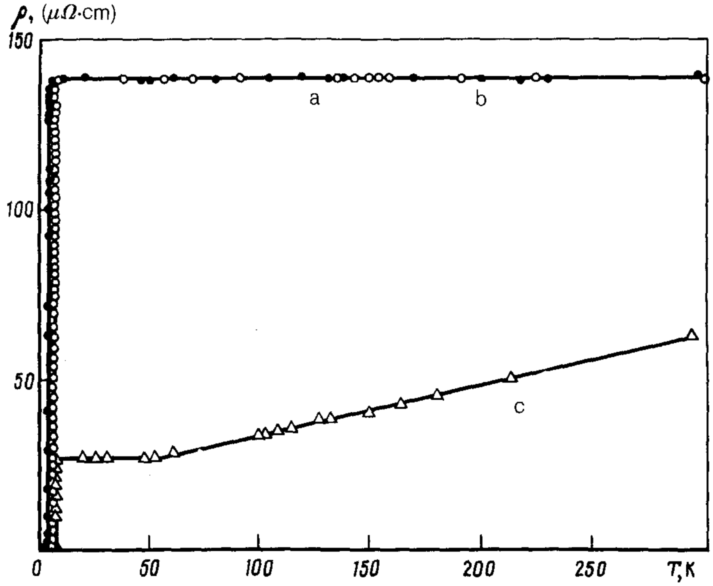

FIG. 1. Temperature dependence of the resistivity ρ of samples of niobium carbide with the composition $NbC_{0.87}$ after heat treatment under various conditions. *a*—Annealing at 1630 K followed by quenching; *b*—annealing at 1360 K followed by quenching; *c*—annealing at 1370 K followed by slow cooling (~5 K/h).

Ref. 3). According to Williams' data,[4] ordered Nb_6C_5 does not superconduct, while Rempel' *et al.*[5] have shown that T_c increases from 2.1 K to 8.3 K as the carbon sublattice becomes ordered. We have made an attempt to determine how the state of the carbon sublattice affects the transition temperature T_c of niobium carbide.

A detailed study was made of niobium carbide with the composition $NbC_{0.87}$. We studied single crystals cut from a large crystal grown by plasma remelting in argon.[6] The resistance of the samples was measured by the dc four-terminal method. The state of the carbon sublattice could be altered by heat treatment of the samples. The heat treatment was carried out in sealed-off quartz cells evacuated to $\sim 10^{-6}$ Torr. The samples were quenched at a rate of 10–20 K/s in air when the cell, with the sample, was removed from the furnace.

Analysis of the experimental data reveals two characteristic temperatures, $T_1 = 1300$ K and $T_2 = 1570$ K, and, correspondingly, three temperature regions in which the heat treatment has different effects on the superconducting properties. Curve *a* in Fig. 1 shows the temperature dependence of the electrical resistivity, $\rho(T)$, of an $NbC_{0.87}$ sample after annealing in the high-temperature region, at $T \approx 1630$ K $> T_2$, and a subsequent quenching. For samples of this type quenched from various temperatures we found $T_c \approx 3.6$–4.2 K; the width of the transition between the 0.1 and 0.9 levels was $\Delta \approx 0.4$–0.7 K; the residual resistivity was high, $\rho(300) = 140\ \mu\Omega\cdot$cm; and the temperature coefficient of the resistivity was nearly zero, $\rho(300)/\rho(4.2) \approx 1$.

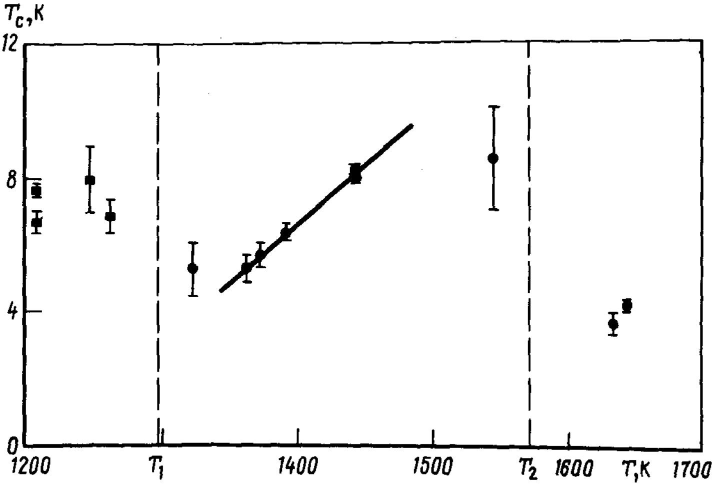

FIG. 2. T_c of the $NbC_{0.87}$ smaples versus the temperature of the heat treatment. ●—Annealing + quenching; ■—annealing + slow cooling (~5 K/h). (The arrow bars show the width of the superconducting transition).

The samples which were subjected to prolonged annealing (2–8 h) in the intermediate temperature range, $T_1 < T < T_2$, and then quenched behave in a completely different way. These samples also exhibit a high and temperature-independent resistivity (curve *b* in Fig. 1), but their T_c depends on the annealing temperature. The highest value, $T_c \approx 8.6$ K, is exhibited by samples held at a high temperature near T_2. Over the entire temperature range $T_1 < T < T_2$ we observe a linear dependence of T_c on the annealing temperature, so that at $T \approx T_1$ we find $T_c \approx 5.3$ K (Fig. 2). At the boundaries of this region, the superconducting transitions become significantly broader.

The superconducting properties of the samples subjected to heat treatment at $T < T_1$ depend strongly on their history. A preliminary annealing in the temperature range $T_1 < T < T_2$, with slow cooling at a rate of 5–10 K/h to $T < T_1$, reduces the resistivity to $\rho(300) \approx 65\ \mu\Omega \cdot$cm and causes a substantial decrease in ρ as the temperature is lowered from room temperature to 10 K: $\rho(300/\rho(10) = 2.45$ (curve *a* in Fig. 1). The superconducting transition temperature of these samples is near 8 K, with $\Delta \approx 0.3$ K (Fig. 2). If the sample is instead annealed at a high temperature $T > T_2$ and then cooled fairly rapidly from T_2 to T_1, the superconducting properties are entirely different. For example, an annealing at 1640 K followed by a cooling to 770 K at a rate of ~100 deg/h leads to a transition temperature $T_c < 1.2$ K, with $\rho \approx 135\ \mu\Omega \cdot$cm and $\rho(300)/\rho(4.2) \approx 1.3$.

Heat treatment of nonstoichiometric niobium carbide at comparatively low temperatures ($T \ll T_m$) thus makes it possible to vary the transition temperature of this material over a wide range. The superconducting properties change in a reversible fashion, so that a given sample can exhibit any transition temperature between $T_c < 1.2$ and $T_c \approx 8.6$ K. To explain such unusual properties of niobium carbide, one might suggest that a restructuring of the carbon sublattice causes a radical change in the phonon spectrum of this carbide. The superconducting electron pairs which are formed by virtue of the electron–phonon coupling should have a binding energy which varies continuously over a wide range. A picture of this sort, however, is improbably. In the first palce, the phonon spectrum of the carbides is determined primarily by the high-energy bonds in the metal sublattice. The heat-treatment temperature is too low to have any significant effect on these bonds or to alter the phonon spectrum of the carbide. Second, prolonged annealing at $T < T_1$ is accompanied by an ordering of the carbon sublattice, and this effect is manifested by a decrease in the resistivity. The interaction of the conduction electrons with the lattice weakens substantially when the carbon sublattice becomes ordered (the mean free path of the electrons increases by a factor ~ 5), while T_c increases by a factor ~ 2 (Fig. 2). Such an increase in T_c would be impossible to explain on the basis of an electron–phonon mechanism for the superconductivity.

Most probably, the pairing occurs in this case as a result of an interaction of conduction electrons with tunneling states formed during a local restructuring of a small group of carbon atoms. Tunnel states are a new class of excitations, which are characteristic of systems with a certain disruption of the order in a small volume.[7] A qualitative explanation of the basic experimental results of the present study can be constructed on the basis of the tunneling model. The density of tunneling states varies with the type of heat treatment, leading to changes in T_c. At $T > T_2$ the carbon atoms move freely through their own sublattice; the tunneling states arise and decay spontaneously and have a low density. At $T = T_2$ (T_2 might be called the "melting point of the carbon sublattice") the formation of tunneling states becomes favored from the energy standpoint, and their density increases sharply. The density of tunneling states is known to be proportional to the temperature of the heat treatment,[8] so this density decreases with decreasing temperature, leading to a decrease in T_c. At $T = T_1$, a long-range order arises, and ordered domains without tunneling states form. The tunneling states can appear only at domain walls, and their density may vary with the type of heat treatment.

In summary, a nonphonon superconductivity mechanism involving an interaction of conduction electrons with the tunneling states which are characterisitc of systems with a disorder may operate in niobium carbide.

[1] S. Nagakura and S. Oketami, Tr. Iron Steel Inst. Jpn. **8**, 265 (1968).
[2] J. P. Landesman *et al.*, J. Phys. C **18**, 809 (1985).
[3] L. E. Toth, *Transition Metal Carbides and Nitrides*, Academic, New York, 1971.
[4] L. C. Dy and W. S. Williams, J. Appl. Phys. **53**, 8915 (1982).
[5] A. A. Rempel' *et al.* Fiz. Tverd. Tela (Leningrad) **28**, 279 (1986) [Sov. Phys. Solid State **28**, 153 (1986)].
[6] E. M. Savitskiĭ *et al.* in *Single Crystals of Refractory and Rare Metals, Alloys, and Compounds*, Nauka, Moscow, 1977, p. 32.
[7] H. J. Gundtherodt and H. Beck, *Glassy Metals*, Springer-Verlag, New York, 1981.
[8] P. W. Anderson *et al.*, Phil. Mag. **25**, 1 (1972).

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