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On the Nature of Superconducting Niobium and Tantalum Monocarbides

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The transition temperatures T_c to the superconducting states of cubic niobium and tantalum carbides in their regions of homogeneity are measured. The electron state band density at the Fermi level $N_0(\epsilon_F)$ and the electron-phonon interaction parameter $V_{ep}$are calculated on the basis of the T_c values and the electron specific heats γ given in the literature. The calculations are performed within the framework of the strong pairing theory. It is shown that the change in T_c is determined by the decrease of both $N_0(\epsilon_F)$ and V_{ep} with increase in the concentration of the carbon vacancies in the carbides under study. The results are used together with data on the concentration-temperature dependences of the magnetic susceptibility to discuss the singularities of the electronic structure of the cubic carbides of the Va subgroup transition metals.

THE cubic niobium and tantalum monocarbides are superconductors with higher superconducting transition temperatures than for the corresponding metals. This has naturally drawn the attention of investigators to them. Their superconductivity has been the subject of a number of publications.[1-3] It has been shown that the transition temperatures of these phases of variable composition decrease rapidly with increase in the concentration x of carbon vacancies. For NbC_{1-x} this circumstance was connected in[2] with a decrease in the parameter of electron-phonon interaction. However, the results of investigations of the concentration dependences of the electronic specific heat[3] and the magnetic susceptibility[4-7] allow us to suppose that these changes in the superconducting transition temperature in regions of homogeneity of the monocarbides are also associated with change in the density of electron states on the Fermi surface, $N(\epsilon_F)$. In this connection, the superconducting transition temperatures, together with other parameters that are sensitive to a change in $N(\epsilon_F)$, can be used for the analysis of the electronic structure of these compounds.

In the present work we report the results of measurements of T_c of the monocarbides NbC_{1-x} and TaC_{1-x} ($0.70 \leq 1 - x \leq 1.0$), carried out on the same specimens on which the concentration-temperature dependences of the magnetic susceptibility were measured previously.[5-8]

The methods of preparation of the samples, the results of their chemical analysis on the metallic content, as well as the content of total and free carbon, oxygen, hydrogen, nitrogen and metallic impurities were given in[5,7]. All the samples were single phase (cubic carbides, with the structure type of NaCl). Their characteristics are given in the table. The measurements of T_c were carried out by the usual induction method described previously.[9]

The data on the electronic specific heats (γ) and the Debye characteristic temperatures (Θ_D) were taken from[3]. The latter were converted according to the results of[3] with account of the presence of two atoms in the primitive cell of the carbides:[10]

$$\Theta_D = \{234 N_A k(2-x)/\alpha\}^{1/3}, \tag{1}$$

where N_A is Avogadro's number, k is Boltzmann's constant, and α is determined from the temperature dependence of the lattice specific heat.

It can be noticed immediately that the concentration dependence of Θ_D, which is obtained in[3] for NbC_{1-x}, is the reverse of what was obtained in[2] (according to the results of[2], Θ_D increases with increase of x in NbC_{1-x}). Evidently, it would be correct to assume a decrease in Θ_D with increase in the concentration of vacancies in the carbon sublattice of the niobium and tantalum carbides,[3] since such a dependence has also been observed in[11], where the Debye temperature of NbC_{1-x} was determined from the elastic constants and obtained from them by means of the empirical formula of Lindemann:

$$\Theta_D = 137\sqrt{\frac{T_m}{Av^{2/3}}}, \tag{2}$$

where T_m is the melting temperature, A is the mean atomic weight, and v is the mean atomic volume. The melting temperature of both NbC_{1-x} and TaC_{1-x} decrease and the mean atomic volumes increase with increase in x. The decrease in the Debye temperatures (by 15–17%) observed in this case cannot, of course, lead to a decrease in T_c by a factor of five within the limits of the regions of homogeneity of the niobium and tantalum monocarbides.

Figure 1 gives our experimental data on the concentration dependences of T_c for NbC_{1-x} and TaC_{1-x}. In general, they are in fair agreement with the results of[1-3].

For estimates of the parameters that determine the observed change in T_c, the band density of states $N_0(\epsilon_F)$ and the parameter of electron-phonon interaction V_{ep} were calculated. Here we have used our data on T_c, the data of[3] on the electronic specific heat, and the equation of McMillan:[12]

$$N_\gamma = N_0(1 + N_0 V_{ep}),$$
$$\frac{1.45 T_c}{\Theta_D} = \exp\left\{-\frac{1{,}04(1 + N_0 V_{ep})}{N_0[V_{ep} - V_C(1 + 0{,}62 N_0 V_{ep})]}\right\}. \tag{3}$$

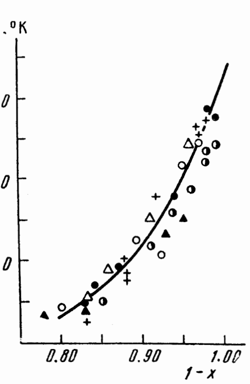

FIG. 1. Effect of composition on the superconducting transition temperature of niobium and tantalum monocarbides: ●—NbC_{1-x}, ○—TaC_{1-x}—data of the authors; +—NbC_{1-x}, ◑—TaC_{1-x}—data of [1]; △—NbC_{1-x}, ▲—TaC_{1-x}—data of [3].

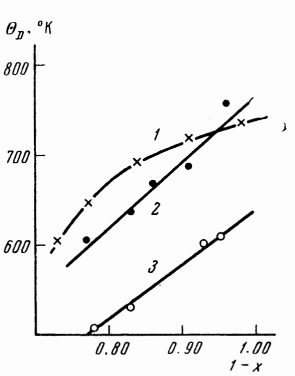

FIG. 2. Debye characteristic temperatures of niobium and tantalum monocarbides: 1—NbC_{1-x}, computed from the elastic constants of [11]; 2—NbC_{1-x} and 3—TaC_{1-x} determined from the calorimetic measurements of [3].

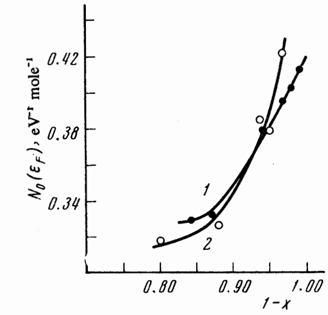

FIG. 3. Band density of electron states of niobium (1) and tantalum (2) moncarbides of various composition; $\mu^* = 0.1$.

McMillan showed that for most polyvalent metals and their alloys, the Coulomb pseudopotential is $\mu^* = N_0(\epsilon_F)V_c = 0.1$ (or a little more.[12]) For example, for lead, the best agreement between the theoretical values of the constant of ep interaction $\lambda = N_0(\epsilon_F)V_{ep}$, computed from (3), and the experimental value, determined from a tunnel experiment, is obtained for $\mu^* = 0.13$. The results of a tunnel experiment on lead serves as an excellent confirmation of the superconducting theory proposed by McMillan.[12] Unfortunately, such experiments are lacking for most metals, alloys, and compounds.

Our calculations were carried out for three values of $\mu^* = 0, 0.1, 0.2$. Here it developed that in all these cases (see the table) the deviation from stoichiometry (both for NbC_{1-x} and TaC_{1-x}) is accompanied by a decrease in $N_0(\epsilon_F)$ by about 20%, and in V_{ep} by 10%. However, recognizing that both these parameters enter exponentially into the equation for T_c, we can understand the observed strong dependence on the concentration of carbon in the carbides.

Figures 2 and 3 give the changes in the Debye characteristic temperature and the band density of states (calculated for $\mu^* = 0.1$) for NbC_{1-x} and TaC_{1-x}. As is seen from these data, the concentration dependence of T_c in the regions of homogeneity of the niobium and tantalum carbides is basically determined both by the change in the constant of ep interaction and by the zone density of states.

The values obtained for $N_0(\epsilon_F)$ were used for the calculation of the paramagnetic susceptibility of the conduction electrons χ_p^- (with accuracy to the first temperature-independent component):

$$\chi_p^- = 2N_A\mu_B^2\left\{N_0(\varepsilon_F) + \frac{\pi^2k^2}{6}\left[N_0''(\varepsilon_F) - \frac{(N_0'(\varepsilon_F))^2}{N_0(\varepsilon_F)}\right]T^2\right\}. \quad (4)$$

It was shown earlier[5,7] that the total experimentally determined magnetic susceptibility for the class of compounds considered is described by the relation

$$\chi_{\text{exp}} = \chi_p^+ + \chi_d^+ + \chi_{vv} + \chi_p^- + \chi_d^-, \quad (5)$$

where χ_p^+ and χ_d^+ are the para- and diamagnetism of the atomic shells M_l and C, χ_{VV} is the Van Vleck polarization paramagnetism, χ_p^- and χ_d^- are the para- and diamagnetism of the conduction electrons, $\chi_d^- = (1/3) \times (m_0/m^*)^2\chi_p^-$, m_0 and m^* the mass of the free electron and the effective carrier mass on the Fermi surface. In the case considered, under the assumption that all the valence electrons of the atoms of the metal and of carbon are collectivized, $\chi_p^+ \equiv 0$. Of all the components of Eq. (5), only χ_p^- is temperature dependent. The weak temperature dependence of $\chi_{\text{exp}}(T)$ (with a change of sign of the temperature coefficient $d\chi_{\text{exp}}(T)/dT$ in the regions of homogeneity of NbC_{1-x} and TaC_{1-x}), observed previously,[5-8] is well described by Eq. (4). This allows us to suppose that the principal contribution to the susceptibility of the carbides is made by the conduction electrons (χ_p^-).

The table gives the values of χ_p^- (calculated by Eq. (4)) and in the next column, $-\chi_{\text{exp}}$, corrected for the diamagnetism of the atomic shells (χ_d^+ is equal to -0.15, -9, -14×10^{-6} emu/mole, respectively for C^{4+}, Nb^{5+}, Ta^{5+}[13]) and extrapolated to 0°K. It should be noted that, in view of the weak dependence $\chi_{\text{exp}}(T)$ for almost all the studied preparations of NbC_{1-x} and TaC_{1-x}, the latter has been obtained with sufficient reliability.

The concentration dependences $\chi_{\text{exp}}(1-x)$ and $\chi_p^-(1-x)$ are shown in Fig. 4. Unfortunately, the data on χ_p^- could be obtained for only three compositions of the carbides, for which $T_c \geq 1.5$°K.

We now turn our attention to the following features:

1) χ_p^- and χ_{exp} are practically identical for stoichiometric composition;

2) upon deviation from stoichiometry ($0 < x \leq 0.2$) both χ_p^- and χ_{exp} decrease but χ_p^- falls off by about 20% while χ_{exp} even changes sign for $x \approx 0.15$, passing through a minimum for $x \approx 0.20$.

These results have value in principle and can be associated with two circumstances:

a) The assumed McMillan theory of superconductivity and Eq. (3) are inapplicable for vacancy structures.

b) Alternately, Eq. (3) is valid even for vacancy

For the calculation of certain characteristics of niobium and tantalum monocarbides

Atomic fraction of C	T_c, °K	Θ_D, °K	γ, MJ-mole^{-1}·°K^{-1}	$N_\gamma(\varepsilon_F)$, eV^{-1}·molec^{-1}	$\mu^* = 0$			$\mu^* = 0.1$			$\mu^* = 0.2$			$\chi_{exp}\cdot10^6$, emu-mole^{-1}
					$N_0(\varepsilon_F)$, eV^{-1}·molec^{-1}	V_{ep}, eV	$\chi_p^-\cdot10^6$, mole^{-1}	$N_0(\varepsilon_F)$, eV^{-1}·molec^{-1}	V_{ep}, eV	$\chi_p^-\cdot10^6$, emu-mole^{-1}	$N_0(\varepsilon_F)$, eV^{-1}·molec^{-1}	V_{ep}, eV	$\chi_p^-\cdot10^6$, emu-mole^{-1}	
							NbC							
0.99	11.18	760	3.00	0.642	0.468	0.79	30.3	0.413	1.34	26.0	0.361	2.16	23.4	28.0
0.98	11.56	754	2.92	0.625	0.454	0.83	29.4	0.401	1.40	25.2	0.346	2.33	22.4	28.8
0.97	10.40	747	2.85	0.610	0.447	0.82	28.9	0.392	1.37	24.9	0.346	2.20	22.4	23.4
0.94	7.30	728	2.65	0.567	0.427	0.77	27.6	0.378	1.32	24.0	0.332	2.13	21.5	21.6
0.87	3.75	678	2.23	0.477	0.374	—	24.2	0.332	1.32	21.2	0.293	2.14	19.0	11.2
0.84	2.85	657	2.18	0.466	0.370	—	23.9	0.329	1.27	21.0	0.290	2.09	18.8	−0.6
0.83	2.00	642	2.16	0.462	0.373	—	24.1	0.331	1.20	21.3	0.293	1.97	19.0	—
0.80	< 1.5	—	—	—	—	—	—	—	—	—	—	—	—	−17.1
0.70	—	—	—	—	—	—	—	—	—	—	—	—	—	13.3
							TaC							
0.97	9.90	621	3.09	0.661	0.478	0.80	30.9	0.422	1.34	26.5	0.369	2.16	23.9	28.4
0.95	8.83	608	2.75	0.588	0.430	0.85	27.8	0.379	1.44	23.9	0.317	2.70	20.5	19.8
0.93	4.15	601	2.65	0.567	0.439	0.66	28.4	0.389	1.18	24.8	0.342	1.92	22.1	13.7
0.88	5.20	569	2.26	0.484	0.368	0.85	23.8	0.326	1.48	20.8	0.286	2.42	18.5	1.1
0.80	1.82	517	2.06	0.441	0.354	0.69	22.9	0.318	1.22	20.1	0.278	2.11	18.0	−13.5
0.74	<1.5	—	—	—	—	—	—	—	—	—	—	—	—	−11.6

structures, χ_p^- changes in correspondence with the curves 1–4 (Fig. 4), and the concentration dependence of the total magnetic susceptibility (curves 5, 6) indicates additional contribution to χ_{exp} besides χ_p^- which, of course, is diamagnetic and changes with the composition of the carbides. Such a contribution can be the diamagnetism of the conduction electrons χ_d^- the value of which can be large for the presence on the Fermi surface of the so-called "small groups" of carriers with small effective masses ($m^* \ll m_0$).

It follows from what has been said that the data considered represent indirect information on the change of the topology of the Fermi surface in carbides of the transition metals of the Va subgroup. For the complex carbides $Me^VC_{1,0}$ the form of the Fermi surface is probably close to spherical, which is characteristic of quasifree electrons; the deviation from stoichiometry materially complicates the topology of the surface, possibly leading to the appearance of hole and electron sheets. The sharp increase in the diamagnetism, as x approaches 0.2 is confirmed and also the anomalies of the temperature dependence $\chi_{exp}(T)$ of these preparations (the so-called "diamagnetic tails," which are due to the sharp increase in the diamagnetism with change in the temperature below 40°K[8]).

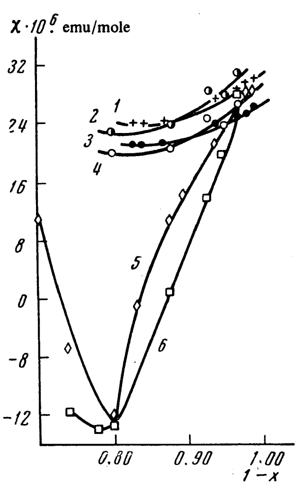

FIG. 4. Isotherms of the magnetic susceptibility of niobium (1 and 3–χ_p- for μ^* equal to 0 and 0.1, respectively; 5–χ_{exp}) and tantalum (2 and 4–χ_p- for μ^* equal to 0 and 0.1 respectively, 6–χ_{exp}) monocarbides.

The considerations stated above agree both with the model of the electron structure of the nonstoichiometric carbides, developed in[14] on the basis of analysis of the concentration-temperature dependences of the kinetic parameters (the Hall constant, electrical resistivity, and the thermal emf). In particular, it has been shown in this work that the kinetic properties of stoichiometric carbides Me^VC are described in the single band model, while the departure from the equi-atom composition leads to the appearance of carriers of both signs; the contribution of the hole carriers increases appreciably near the given critical composition ($MeC_{0,80}$).

So far as the Van Vleck paramagnetism is concerned, it can be said that in all probability it is close to zero for complex lattices MeC with face-centered cubic symmetry. Departure from stoichiometry, which lowers the symmetry of the electron clouds, should evidently produce some increase of it. However, our results show that this contribution is of second order in all compositions.

The calculations of the electron spectra of the carbides Me^VC with complex lattices (VC, NbC, TaC)[15] have also shown that the Fermi level (ε_F) in them is located in the Me-Me band, which is above the upper edge of the Me-C band. Direct experiments on the determination of the topology of the Fermi surface of stoichiometric and nonstoichiometric carbides are desirable, and also theoretical calculations of the band structure of nonstoichiometric carbides.

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