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Ab Initio Calculations of the Superconducting Transition Temperature for NbC at Various Pressures

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Ab initio calculations of the superconducting properties have been performed for niobium carbide (NbC) at normal pressure and upon a 15 and 30% compression. Factors accounting for the relatively low values of the transition temperature T_c in transition metal carbides are considered and the possible ways of increasing this parameter are discussed. *© 2004 MAIK "Nauka/Interperiodica".*

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According to the Bardeen–Cooper–Schrieffer (BCS) theory, the maximum critical temperature T_c of the superconducting transition might be observed in metals possessing minimum atomic masses M, since this theory predicts that $T_c \sim 1/M^{1/2}$. For this reason, much attention was devoted for many years to the possible superconductivity of metallic hydrogen (see, e.g., review [1]). The results of our recent *ab initio* calculations [2] showed that metallic hydrogen at ultrahigh pressures ($p \sim 20$ Mbar) might actually be a superconductor with $T_c \sim 600$ K. Unfortunately, not only practical use but even the synthesis of superconducting metallic hydrogen at such pressures is impossible. The possibility of reaching high T_c values was previously also considered for metal hydrides. Recently, Ashcroft [3] returned to this problem in the context of the revival of the general interest in searching for new high-T_c compounds exhibiting superconductivity in the intermediate temperature range.

In addition to metal hydrides, of considerable interest from the standpoint of reaching high T_c values are transition metal borides, carbides, nitrides, and oxides, because they are also characterized by quite high frequencies of optical phonons associated predominantly with the vibrations of light atoms. One of such compounds, possessing a relatively high transition temperature ($T_c \sim 40$ K), is magnesium diboride (MgB_2) [4], in which superconductivity is primarily due to the interactions between optical vibrations and electrons localized at the boron sites. As is known, T_c depends both on the atomic mass and, which is even more significant, on the constant of the electron–phonon interaction for a given phonon mode.

In this context, we apply the methods of *ab initio* calculations reported in [5, 6] to study superconductivity in niobium carbide (NbC) so as to elucidate the causes for the relatively low critical temperature ($T_c \sim 11$ K) and to determine the T_c change with increasing pressure.

Previously, transition metal carbides and nitrides were also considered as potential high-T_c materials [7, 8]. In these investigations, the electron–phonon interaction constants for these materials were qualitatively assessed and it was shown that $T_c \approx 30$ K might be expected in MoN. However, the calculations were performed for stoichiometric MoN with a structure of the NaCl type. Unfortunately, such a structure is never realized for the stoichiometric composition and can be stable only in MoN_{1-x} with $x \geq 0.3$.

Complete microscopic calculations of the electron and phonon spectra of transition metal carbides and nitrides and their electron–phonon interaction constants were almost not performed because of considerable difficulties. One of a few examples is offered by *ab initio* calculations of the phonon spectra of NbC [9] by the full-potential inear muffin-tin orbital method (FP-LMTO) [5]. In the present study, calculations were performed (like those in [2, 6, 9]) using the program package implementing the FP-LMTO method as described in [5].

Figure 1 shows the density of states (DOS) $N(E)$ calculated for NbC at $V = V_0$ (V_0 is the specific volume at atmospheric pressure) and at $V = 0.85V_0$ and $0.70V_0$ (that is at a 15 and 30% lattice compression, respectively). The compressibility of NbC is relatively small (the bulk modulus is $K_{NbC} = 340$ GPa) and these compressions correspond to a pressure of $p \sim 0.6$ and 1.5 Mbar, respectively. In Fig. 1, the $N(E)$ peak at an energy of ~0.2 Ry above the Fermi level (E_F) is due to the unoccupied Nb 4d states. The peak at ~0.3 Ry below E_F is mostly due to the C 2p states hybridized with the occupied Nb 4*d* states. A structure in the region of energies about –1 Ry is formed by the so-called "semi-core" 4*p* states of niobium. At normal pressure, the shape of $N(E)$ agrees well with the results of previous DOS calculations for NbC [7, 8]. As can be seen from Fig. 1, it is most likely that an increase in pressure reduces T_c, because $N(E)$ at the Fermi level decreases in this case.

We have also calculated the phonon spectra $\omega(\mathbf{q})$ and the spectral density of the electron–phonon interaction (the Eliashberg function) for NbC in all the cases under consideration. The Eliashberg function $\alpha^2(\omega)F(\omega)$ for NbC at various pressures is shown in Fig. 2. The phonon DOS is not depicted in this figure because the shape of this curve is very similar to that of $\alpha^2(\omega)F(\omega)$. As is seen in Fig. 2, the Eliashberg function (as well as the phonon DOS) consists of two peaks significantly spaced on the frequency scale. The low-frequency peak describes the interaction of electrons with acoustic phonons, while the high-frequency peak refers to the interaction with optical phonons. The coupling constants for the corresponding phonons were calculated using the formula

$$\lambda_{\mathrm{ph}} = 2\int_{\omega_1}^{\omega_2} \frac{d\omega}{\omega}\alpha^2(\omega)F(\omega). \qquad (1)$$

Integrating in Eq. (1) from $\omega_1 = 0$ to $\omega_2 = 14$ THz (see Fig. 2), we obtain the constant of coupling with the acoustic phonons (λ_{ac}). At normal pressure and 15 and 30% compressions, this calculation yields $\lambda_{\mathrm{ac}} = 0.71$, 0.50, and 0.35, respectively; the constants of coupling with the optical phonons at the same pressures are much lower: $\lambda_{\mathrm{op}} = 0.21$, 0.19, and 0.16, respectively.

Within the framework of the simple "rigid muffin-tin" approximation used in the early investigations [7, 8], the coupling constant λ for binary compounds AB with substantially different ion masses can be expressed as

$$\lambda = \lambda_{\mathrm{ac}} + \lambda_{\mathrm{op}} = \frac{N_A(0)\langle I_A^2\rangle}{M_A\langle\omega_A^2\rangle} + \frac{N_B(0)\langle I_B^2\rangle}{M_B\langle\omega_B^2\rangle}, \qquad (2)$$

where $N(0)$ is the DOS at the Fermi level and $N(0)\langle I^2\rangle$ is the Hopfield parameter [10], which is proportional to the square of the matrix element of the electron–phonon interaction integrated over the Fermi surface. According to estimates [11], carbides obey the relation

$$M_A\langle\omega_A^2\rangle \cong M_B\langle\omega_B^2\rangle. \qquad (3)$$

The Hopfield parameter for Nb and C atoms was also calculated in [11], where the value for carbon has proved to be less than half of that for niobium. We have performed more precise calculations, which showed that, first, the constant of coupling with the optical modes is less than one-third of that for the acoustic modes and, second, our values of the constant of coupling with the acoustic modes are about twice as large as those obtained in [11]. Qualitatively, the smaller values of λ_{op} obtained in [11] and in our calculations are explained by a low DOS for the carbon-bound electrons on the Fermi surface. The chemical bonds in NbC are predominantly ionic: electrons from Nb pass to the C 2*p* states occurring 0.3–0.35 Ry (4–5 eV) below the Fermi level, and only small tails of these states emerge at the Fermi surface.

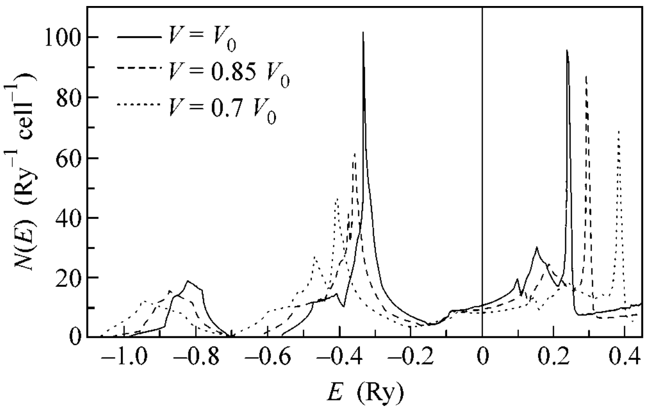

Fig. 1. DOS profiles $N(E)$ for NbC at normal pressure and upon 15 and 30% compression ($p \sim 0.6$ and 1.5 Mbar, respectively). V_0 is the equilibrium specific volume at $p \approx 0$. The energy is measured relative to the Fermi level.

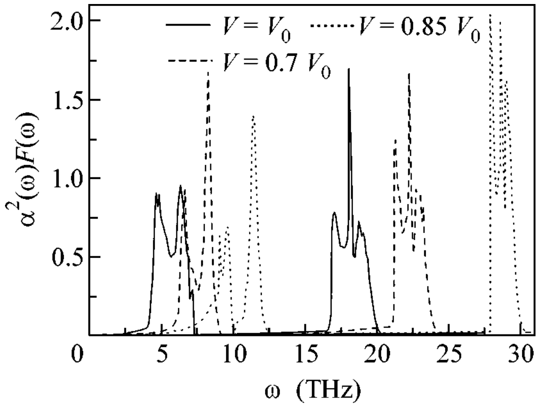

Fig. 2. Eliashberg function $\alpha^2(\omega)F(\omega)$ for NbC at normal pressure ($p \approx 0$) and upon 15 and 30% compression.

According to the results of our calculations, an increase in the pressure leads to a decrease in the DOS $N_{\mathrm{Nb}}(0)$ associated with the niobium states at the Fermi level, while the DOS $N_{\mathrm{C}}(0)$ associated with the carbon states at the Fermi level remains virtually unchanged. Increasing pressure leads to a sharp increase in the phonon frequency in both optical and acoustic branches. For a compression corresponding to $V = 0.7V_0$, the $M\langle\omega^2\rangle$ value increases by a factor of 2.5 and

2.3 for the optical and acoustic modes, respectively. At the same time, the coupling constant λ_{op} exhibits only a 25% decrease rather than a severalfold drop, as it might be expected from formula (2) for $\langle I^2 \rangle$ = const. This behavior implies that the growth of the pressure is accompanied by an increase in the matrix element of the electron–phonon interaction at the carbon atom. The acoustic coupling constant is halved; that is, it decreases approximately to the same extent to which the $M_{Nb}\langle \omega_{Nb}^2 \rangle$ value increases.

The superconducting transition temperature T_c can be determined by solving the Eliashberg equation [12] with the known function $\alpha^2(\omega)F(\omega)$. With neglect of the Coulomb repulsion, these calculations give T_c = 15.7 K for NbC. However, such *ab initio* calculations do not allow the Coulomb contribution to T_c to be estimated. For this reason, we have determined the Coulomb pseudopotential μ^* from the condition of coincidence of the calculated and experimental T_c values (T_c^{exp} = 11.1 K), which yields μ^* = 0.15. This value is likely to be somewhat overstated, since our calculations were performed for the stoichiometric NbC, while the real compound usually exhibits a deficiency of carbon. It is also known [7] that the transition temperature in NbC_{1-x} quite rapidly drops with increasing x. According to the results of our calculations, T_c also decreases rapidly with increasing pressure: T_c = 4.9 K for a 15% compression and T_c = 0.98 K for a 30% compression (the calculations were performed for the same pseudopotential μ^* = 0.15).

The good accuracy of our calculations of the Eliashberg function and coupling constants is confirmed by the following fact. We have calculated the transport Eliashberg function $\alpha_{tr}^2(\omega)F(\omega)$ and the electron–phonon interaction contribution to the resistivity ρ of NbC (the method of calculation is described in [5, 6]). At room temperature (T = 273 K), the calculated resistivity is ρ = 18.1 $\mu\Omega$ cm. The measurements of resistivity for a nearly stoichiometric niobium carbide $NbC_{0.98}$ [13] showed a rather high residual value of ρ_0 = 24 $\mu\Omega$ cm. When the temperature was changed from low values to 300 K, the resistivity increment amounted to ρ_{ph} = 15.5 $\mu\Omega$ cm. This value is very close to the result of our calculation (the difference is less than 20%). Taking into account that, for such a high value of ρ_0, Matthiessen's rule of the simple additivity of the residual and temperature-related contributions to the resistivity may itself be violated to within 20%, the obtained agreement between the calculated and experimental values of the resistivity can be considered as quite satisfactory.

Returning to our analysis of the possibility of reaching relatively high T_c values in transition metal carbides, it is possible to describe the situation as follows. According to formula (2), the electron–phonon interaction constant is determined to a considerable extent by the DOS at the Fermi level. For ZrC, NbC, MoC, and MoN systems with a cubic structure, $N(E)$ is well described using the "rigid band" approximation [14], that is, by simply shifting the Fermi level position. In ZrC, the number of electrons per unit cell is lower by one than that in NbC and, accordingly, the Fermi level is situated approximately 0.15 Ry (about 2 eV) lower and falls within a minimum in the DOS (see Fig. 1). In agreement with this picture, ZrC is not a superconductor. In NbN, where the number of valence electrons is greater by one than that in NbC, the Fermi level shifts rightward to higher DOS values. Accordingly, this compound is characterized by a higher transition temperature (T_c = 17 K). In MoN, E_F shifts rightward to an even greater extent, since the number of electrons per unit cell is greater by two than that in NbC. The DOS at the Fermi level in MoN is almost twice that in NbC. As was noted above, in accordance with the estimates obtained in [7], the transition temperature in MoN must be on the order of 30 K, although the experimental value is much lower. The fact is that this compound was never obtained with the stoichiometric composition and real samples always exhibited a deficiency of nitrogen. It was pointed out [14] that the cubic MoN phase is dynamically unstable and only the presence of nitrogen vacancies can stabilize this phase.

An even a more promising way of obtaining high T_c values would be the synthesis of carbides having the number of electrons per unit cell smaller by one than that in ZrC. An example could be offered by yttrium carbide with a structure of the NaCl type, where a situation (now purely hypothetical) might take place in which the Fermi level would fall within a peak in the DOS at 0.33 Ry (~4.5 eV) below E_F in NbC. In this energy region, the DOS is already sufficiently high, but it is even more important that, after such a rigid energy shift, the C 2p states strongly hybridized with the Y 5d states emerge directly at the Fermi level. However, it should be taken into account that it is the high value of $N(0)$ in MoN [14] that accounts for the instability of the cubic phase of this compound. In all probability, a cubic structure of the NaCl type is not more readily achieved in the stoichiometric YC. Moreover, a high concentration of carbon vacancies renders yttrium carbide either a poor metal (with a low density of carriers) or even a semiconductor [15].

It should be noted that, nevertheless, these are yttrium carbides in which record high T_c values have been observed. In particular, the transition temperature in Y_2C_3 is 18 K [16], while that in yttrium borocarbides reaches a level of 15–23 K [17]. In any case, the search for superconductors with relatively high T_c values (~40–50 K) among the compounds of metals with light elements is very interesting from the basic standpoint and important for practical applications.

At present, there are quite realistic projects for using the superconducting compound MgB_2, which offers considerable technological advantages in comparison, for example, with high-T_c cuprates. Metal nitrides and carbides may be even more promising materials in this respect, provided that samples with transition temperatures on the order of ~40 K will be synthesized.

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REFERENCES

1. E. G. Maksimov and Yu. I. Shilov, Usp. Fiz. Nauk **169**, 1223 (1999) [Phys. Usp. **42**, 1121 (1999)].
2. E. G. Maksimov and D. Yu. Savrasov, Solid State Commun. **119**, 569 (2001).
3. N. W. Ashcroft, Phys. Rev. Lett. **92**, 187002 (2004).
4. J. Nagamatsu, N. Nagakawa, N. Muranaka, *et al.*, Nature **410**, 63 (2001).
5. S. Yu. Savrasov and D. Yu. Savrasov, Phys. Rev. B **46**, 12181 (1992).
6. E. G. Maksimov, S. Yu. Savrasov, and D. Yu. Savrasov, Usp. Fiz. Nauk **167**, 337 (1997) [Phys. Usp. **40**, 317 (1997)].
7. W. E. Pickett, B. M. Klein, and D. A. Papaconstantopoulos, Physica (Amsterdam) **108**, 667 (1981); D. A. Papaconstantopoulos, W. E. Pickett, B. M. Klein, *et al.*, Nature **308**, 494 (1984).
8. Y. Zho and S. Hes, Solid State Commun. **45**, 281 (1983).
9. S. Yu. Savrasov, Phys. Rev. B **54**, 16470 (1996).
10. J. J. Hopfield, Phys. Rev. **86**, 443 (1969).
11. B. M. Klein and D. A. Papaconstantopoulos, Phys. Rev. Lett. **32**, 1193 (1974).
12. G. M. Éliashberg, Zh. Éksp. Teor. Fiz. **39**, 1437 (1961) [Sov. Phys. JETP **12**, 1000 (1961)].
13. C. Y. Allison, F. A. Modine, and R. H. French, Phys. Rev. B **35**, 2573 (1987).
14. L. Gus, W. Hart, and B. M. Klein, Phys. Rev. B **61**, 3151 (2000).
15. T. Ya. Kosolapova, *Structure, Production, and Application of Refractory Carbides* (Metallurgizdat, Moscow, 1986) [in Russian].
16. G. Amano, S. Akutagawa, T. Muranaka, *et al.*, J. Phys. Soc. Jpn. **73**, 530 (2004).
17. R. J. Cava, H. Takagi, N. W. Zandbergen, *et al.*, Nature **367**, 252 (1994).

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