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Anomalously enhanced superconductivity and *ab initio* lattice dynamics in transition metal carbides and nitrides

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The lattice dynamics for the monocarbides and mononitrides of the early transition metals has been studied using first-principles density functional perturbation theory. It is shown that the superconductivity of transition metal carbides is directly related to anomalies in the phonon spectra which in their turn are connected to the number of valence electrons. The calculated electron-phonon interaction constants are in excellent agreement with experimental data. Superconductivity is considerably enhanced for substitutional MC_xN_{1-x} alloys. We also predict that perfect VC in the sodium chloride structure ($B1$) is a superconductor with a transition temperature T_c=11.5 K. The experimental failure to sythesize some transition metal carbides and nitrides within the $B1$ structure is connected to their dynamical instability.

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Transition metal carbides (TMC's) and nitrides (TMN's) are extremly hard metallic compounds with very high melting temperatures.[1] For instance, the melting temperature of 4200 °C for TaC is the highest among known materials. These properties are connected to the lattice dynamics of TMC's and TMN's. Besides, they are chemically stable and have high corrosion resistance. Due to these technologically important properties, they are widely used in industry—e.g., as dispersion hardening particles in high-speed steels for cutting tools. The lattice dynamics properties of transition metals and their compounds have been reviewed in Ref. 2. Experimental investigations of the phonon spectra of TMC's (NbC, HfC, and TaC) (Ref. 3), revealed pronounced anomalies in the phonon dispersion curves for NbC and TaC, but the spectrum for HfC, which is not a superconductor, at least for $T>1$ K, did not show any anomalies. This suggested that the superconductivity of TaC is connected to its anomalous phonon spectrum. It was also shown that phonon anomalies are related to pecularities of the band structure. Indeed, nesting of flat portions of the Fermi surface sheets was observed in TaC and NbC,[4,5] but for HfC strong flat sheets of the Fermi surface were not found.[5] The phonon dispersion relations in TiC and the influence of carbon vacancies on the spectrum have been studied using inelastic neutron scattering.[6] The measured spectrum for TiC (Ref. 6) and phonon spectra for a number of TM carbides (ZrC, NbC, TaC, HfC, and UC) have been investigated within the phenomenological "double-shell" model[7] (DSM) where long-range interatomic interactions were taken into account in order to get a reliable agreement with experimental dispersion curves. The effects of strong phonon anomalies and electron-phonon interactions on the transport properties of TMC's and TMN's have been studied in Refs. 8 and 9 using the strong-coupling theory of superconductivity. Inelastic neutron scattering experiments have shown that the phonon spectra of NbC (Ref. 3), TaC (Ref. 3), TiN (Ref. 10), ZrN (Ref. 11), and HfN (Ref. 11) display a large dip in the longitidunal acoustic (LA) mode along the high-symmetry $[q00]$ and $[qq0]$ directions, as well as a softening of both the LA and transversal acoustic (TA) modes near the L point. Pressure-induced changes in phonon-related properties, such as the Debye temperature, electron-phonon coupling constant, and superconducting temperature of HfN, ZrN, and NbN, have been studied by means of Raman-scattering measurements.[12] Another intriguing fact is that some transition metal carbides and nitrides have never been synthesized experimentally in the cubic $B1$ structure—for example, MoC and MoN. This behavior has been suggested to be related to a phonon instability at the X point.[13] Earlier, the increase of the density of states at the Fermi level gave a rise to a suggestion that MoN is a candidate for $T_c \sim 30$ K.[14,15] *Ab initio* phonon calculations for NbC (Ref. 16) and TiC (Ref. 17) have been done using the linear response method and linear muffin tin orbitals (LMTO's) as basis functions and in the framework of the supercell method in conjunction with norm-conserving pseudopotentials and plane waves, respectively.

In this paper, we report systematic results of *ab initio* phonon calculations for the TMC's and TMN's, and investigate the connection between anomalies of phonon spectrum and their superconducting properties, as well as the lattice stability as a function of the number of valence electrons. Our calculations are done within the framework of the density functional perturbation theory[18] and the harmonic approximation to force constants using ultrasoft pseudopotentials[19] and plane waves. Exchange-correlation effects were treated using the generalized gradient approximation.[20] Integration over the Brillouin zone was performed by means of Monkhorst-Pack special points[21] using the $16\times16\times16$ k mesh, while electron-phonon coupling constants were calculated using the $24\times24\times24$ k mesh, and averaged on $6\times6\times6$ q points. The phonon spectra for TMC and TMN studied were obtained using 29 force-contstant

TABLE I. Calculated ground-state parameters for TMC's and TMN's within $B1$ structure. The lattice constant a is given in Å; bulk modulus B is in GPa. Experimental values are shown in parentheses.

Compound	a	B
TiC	4.36 (4.3176,[a] 4.326[b])	242 (239,[c] 240,[d] 233[e])
ZrC	4.699 (4.6957[a])	222 (265[b])
HfC	4.651 (4.638[a])	238
VC	4.154 (4.1599[a])	304 (303[b])
NbC	4.476 (4.47[a])	301 (315[b])
TaC	4.47 (4.44[a])	324 (321,[b] 332[d])
TiN	4.275 (4.239[a])	264 (288[e])
ZrN	4.5826 (4.585[a])	250 (215[f])
HfN	4.54 (4.52[a])	269 (306[f])

[a]Reference 22.
[b]Reference 23.
[c]Reference 24.
[d]Reference 25.
[e]Reference 26.
[f]Reference 27.

matrices. Results of ground-state parameters calculations for TMC's and TMN's are summarized in Table I, and we found good agreement between the theory and experiment. The electron-phonon coupling constant λ is calculated by means of the Eliashberg spectral function $\alpha^2F(\omega)$, and then the modified McMillan equation is used to evaluate the superconducting temperature T_c.

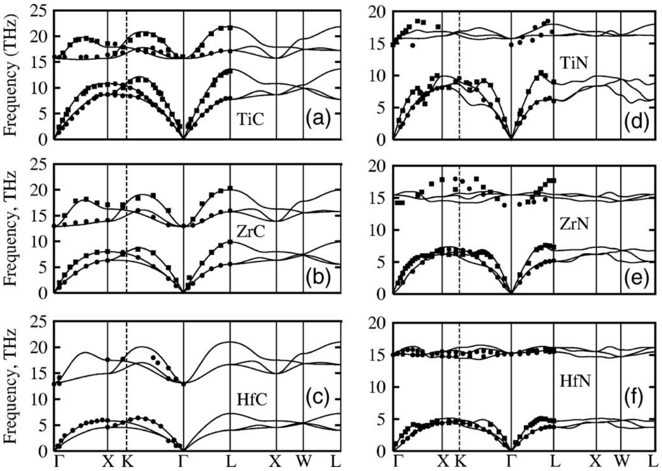

FIG. 1. Phonon spectra of IV^b group metal carbides and nitrides along high-symmetry directions in the Brillouin zone. Experimental points for TiC (a), ZrC (b), HfC (c), TiN (d), ZrN (e), and HfN (f) are taken from Refs. 6, 3, 10, and 11, respectively. Bold circles refer to transversal modes, and squares stand for longitidunal modes.

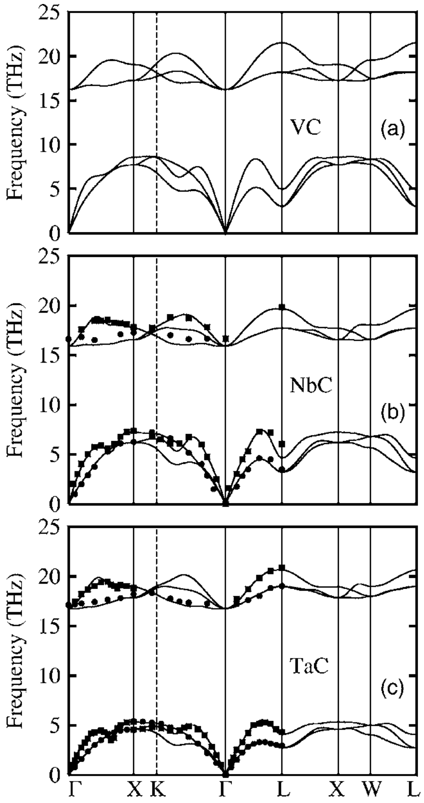

FIG. 2. Phonon dispersion relations for $B1$ VC (a), NbC (b), and TaC (c) along high-symmetry directions in the Brillouin zone. Experimental points for NbC and TaC are taken from Ref. 3.

First, we present the calculated phonon spectra for the IV^b group metal carbides [see Figs. 1(a)–1(c)]. There is an excellent agreement between our present *ab initio* results and the experimental results for the TMC's. The acoustic phonon branches do not possess any anomalies and are similar to those for noble metals with fcc lattices which are in fact not superconductors. In contrast the acoustic branches of the mononitrides [Figs. 1(d)–1(f)] show phonon anomalies in all [100], [110], and [111] directions. There is a dip of the LA mode along the [100] direction (near $q \approx 0.7$) and a softening of both the LA and TA modes along the direction [110]. For TiN a pronounced softening of the LA mode near the L point also takes place, but the softening for ZrN and HfN is rather weak compared to TiN in accordance with experimental results.[10,11] For V^b group metal monocarbides and mononitrides within the $B1$ structure, we have found new features. In contrast to the III^b and IV^b group metal carbides acoustic modes of VC, NbC, and TaC have anomalous phonon spectra features. The phonon dispersion relations for VC [Fig. 2(a)] were not compared to experiment, because VC is highly nonstoichiometric and to the best of our knowledge there was no publication devoted to experimental synthesis and study of the lattice dynamics of stoichiometric VC. For NbC [Fig. 2(b)] and TaC [Fig. 2(c)] we have found excellent agreement between the theoretical and experimental spectra. The observed anomalies are a dip of the LA mode in the [100] direction and a softening of both the LA and TA modes along the [110] and [111] directions. Compared to IV^b group metal mononitrides pecularities of the spectra for VC, NbC, and TaC are not considerably suppressed upon increasing atomic number and a softening of the LA and TA modes near the L point is more pronounced. We keep in mind that the monocarbides NbC and TaC are superconductors with $T_c = 11$ K and 10 K, respectively.[1] Our calculated phonon spectrum for NbC reveals anomalies of the spectrum along both the [q00]

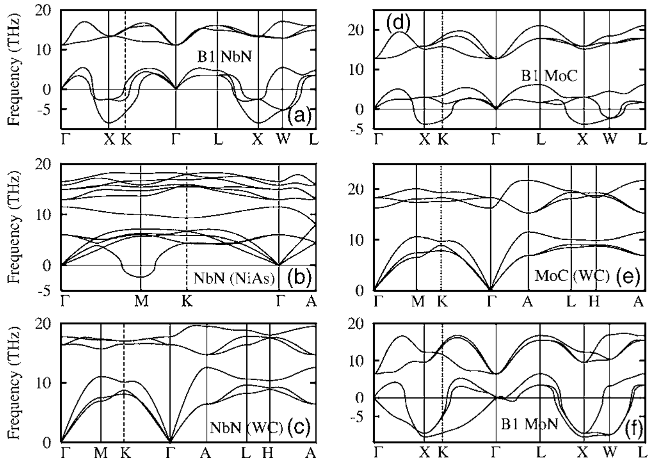

FIG. 3. Phonon spectra for NbN, MoC, and MoN along high-symmetry directions in the Brillouin zone. Left panel: *B*1 NbN (a), NbN within hexagonal NiAs (b), and WC (c) structure type. Right panel: *B*1 MoC (d), MoC within hexagonal WC (e), and *B*1 MoN (f) structure type.

and $[qq0]$ directions, in contrast to the *ab initio* calculations in Ref. 16, where pecularities of the calculated phonon spectrum along the high-symmetry $[qq0]$ direction are not so pronounced.

In order to study the dynamic stability of V^b group metal mononitrides with ten valence electrons, we have calculated the phonon dispersion relations for the nitrides, and we present phonon spectrum only for NbN [see Fig. 3(a)]. Here we have found imaginary frequencies along the high symmetry Γ-X direction. Therefore, this system is dynamically unstable and cannot be crystallized in the NaCl-type structure. From Fig. 3(b), one can see that the phonon spectra of NbN in the NiAs-type structure also has an imaginary frequency near the M point. This is in sharp contrast to NbN with a WC-type lattice which shows no anomalies in any directions [Fig. 3(c)]. Therefore, NbN will adopt the WC-type structure.[28] We can now ask ourselves why *B*1 MoC and MoN were never synthesized experimentally.[13] In order to identify the origin of this failure, we analyzed their phonon spectra and found that [Figs. 3(d) and 3(f)] the spectra for *B*1 MoC and MoN possess imaginary frequencies. Accordingly, they are dynamically unstable, thus explaining the failure to produce *B*1 MoC and MoN. Furthermore, our results for the phonons for MoC within the hexagonal WC-type structure [Fig. 3(e)] show that there are no anomalies in the acoustic modes and hence the stoichiometric MoC can crystallize in the WC-type structure. Note that in Ref. 29 a drastic decrease of the C_{44} elastic constant for VN with respect to the number of valence electrons was interpreted as a precursor for an elastic instabilty. Moreover, MoN with 11 valence electrons in the unit cell was found[30] to be unstable with respect to orthorhombic and trigonal distorsions in agreement with our conclusion about the lattice instability of *B*1 MoN. Besides this, MoC and MoN were found to be elastically unstable[13] and MoN and CrN with 11 valence electrons could not crystallize in the NaCl structure.[29]

Based on the results of our calculations of the phonon spectra for III^b-VI^b group TMC's and TMN's containing from 7 up to 11 electrons in the *B*1 lattice type, we have concluded that TMC's and TMN's containing up to 9 valence electrons are dynamically stable, but in the case of 10 and more valence electrons they are dynamically unstable, and a phase transition should be expected. Besides, the acoustic modes of the phonon spectra of TMC's and TMN's with 8 valence electrons do not contain any anomalies in contrast to other considered number of valence electrons in the unit cell. The same conclusion was applied to NbN and MoC for which we have shown that they should adopt the hexagonal WC-type structure. It was also applied to *B*1 TiO and ZrO,[31] and it turned out that both oxides are also dynamically unstable, confirming our suggestion. It is very exciting to note that two very different compounds, like TiO and MoC, show the same behavior due to their isoelectronic structure. So far Weber,[7] based on a very limited number of experimental results, stated that TaC and NbC, as well as TiN, ZrN, and HfN, with 9 valence electrons[1,7] show significant phonon anomalies; therefore, they are superconductors. The pseudobinary $\mathrm{NbC}_{0.3}\mathrm{N}_{0.7}$ and $(\mathrm{NbN})_{0.8}(\mathrm{TiC})_{0.2}$ systems with almost 10 valence electrons have $T_c \sim 18$ K; however, they are unstable and undergo phase transitions.[1]

In order to show the relation between phonon anomalies and superconductivity, we have studied the electron-phonon interaction (EPI) constants in isoelectronic TMC's and TMN's with nine valence electrons in the unit cell and found excellent agreement with λ evaluated from experimental T_c using the McMillan equation with a reliable Coulumb pseudopotential μ^* (see Table II). For VC we used $\mu^* = 0.12$, close to a conventional value (0.1–0.13), but for other TMC's and TMN's, μ^* was chosen in order to get an agreement with available experimental temperature. It is interesting to note that the calculated λ for TMC's and TMN's vary in a narrow range 0.59–0.67 and 0.78–0.87 for the nitrides and carbides, respectively, which reflects the similarity of the pecularities of their phonon dispersion relations. Indeed, the shape of the spectra for isoelectronic TMC's and TMN's with nine valence electrons in the unit cell is similar, and the observed difference could be ascribed to the presence of nonmetal vacancies and different atomic masses for TM's. For example, the largest dip at $q \approx (0.7, 0, 0)$ is observed in $\mathrm{TiN}_{0.98}$ with 2% nitrogen vacancies, but for the HfN samples which contained up to 6% of nonmetal defects, the dip along the $[100]$ direction is considerably smeared out. It is worth noting that nonstoichiometric $\mathrm{TiN}_{0.98}$ has a lower T_c (5.49 K), and as a result the evaluated $\lambda = 0.54$ is lower[7] compared to 6.0 K, and $\lambda = 0.59$ for a more perfect $\mathrm{TiN}_{0.995}$ sample.[32] For $\mathrm{TiN}_{0.95}$, T_c is considerably reduced down to 1.7 K, and moreover, for $x \leqslant 0.8$ TiN_x becomes nonsuperconducting at least at temperatures above 1.5 K.[32] Stoichiometric or even nearly stoichiometric VC and VN samples were never reported experimentally, and no data are available concerning their lattice dynamics and superconductivity. Nevertheless, we predict that perfect stoichiometric VC crystals should be superconducting with $T_c \sim 11.5$ K and $\lambda \approx 0.78$. Substoichiometric $\mathrm{VC}_{0.88}$ was reported to be nonsuperconducting material,[7] and, obviously, it tends to behave as vacancy-rich TiN_x.

Taking into account that TMN's of V^b group metals are dynamically unstable, but that their carbides are stable, we

TABLE II. Calculated electron-phonon coupling constants and superconducting transition temperature for isoelectronic IV^b group metal nitrides and V^b group carbides with nine valence electrons in the unit cell.

	$\lambda^{calc,\mathrm{a}}$	λ^{expt}	$\mu^{*,\mathrm{a}}$	μ^*	$\omega_{log}^{\mathrm{a}}$(K)	$T_c^{calc,\mathrm{a}}$ (K)	T_c^{expt} (K)
TiN	0.59	0.59,[b] 0.54[c]	0.145	0.11[b]	470	6.0	6.0,[b] 5.49[c]
ZrN	0.66	0.67,[c] 0.627[d]	0.12	0.11[d]	402	10.1	10.0[c]
HfN	0.67	0.69,[c] 0.643[d]	0.115	0.11[d]	323	8.9	8.83[c]
VC	0.78		0.12		327	11.5	
NbC	0.87	0.66–0.72[c] 0.63[e]	0.18	0.13[e]	340	10.5	11.2[c]
TaC	0.78	0.925,[f] 0.72[c]	0.12	0.1[f]	272	10.4	10.6,[f] 10.35[c]

[a] This work.
[b] Reference 32.
[c] Reference 7.
[d] Reference 12.
[e] Reference 33.
[f] Reference 9.

suggested that higher T_c could be obtained by N substitution of C atoms in TMC's (or vice versa). Indeed, using the virtual crystal approximation, we have found that λ for the substitutional $M\mathrm{C}_x\mathrm{N}_{1-x}$ ($M=\mathrm{V,Nb,Ta}$) alloys are considerably increased. For example, λ for $\mathrm{NbC}_{50}\mathrm{N}_{50}$ is larger by a factor of 1.75 compared to the perfect carbide. Using $\lambda=1.52$ and $\mu^*=0.13$ resulted in $T_c\approx 24$ K for $\mathrm{NbC}_{50}\mathrm{N}_{50}$. This value is larger than the experimental $T_c\approx 16$ K (Ref. 33) and this discrepancy could be ascribed to the presence of defects in experimental samples.

We should remark that in our calculations anharmonic terms are not taken into account. Actually, anharmonic effects are small for TaC and NbC, but could be important for $\mathrm{TaC}_{1-x}\mathrm{N}_x$ and NbN.[8] Ultrasonic experiments for elastic and nonlinear acoustic properties revealed that acoustic-mode anharmonicity is small for both TiC and TaC. Anharmonicity might stabilize phonons near the critical points, but it is questionable taking into account the large value of imaginary frequencies.

In conclusion, we have shown that superconductivity of some TMC's and TMN's is connected to anomalies in the acoustic modes of their phonon spectra. The calculated electron-phonon coupling constants for the TMC's and TMN's are in very good agreement with available experimental data. We have also shown that the reason for the experimental failure to synthesize a number of stoichiometric TMC's and TMN's within $B1$ structure is related to phonon instabilities. Besides, we have concluded that the lattice stability of TM carbides and nitrides, as well as oxides, is strongly affected by the total number of valence electrons in systems. We predict that stoichiometric defect-free VC crystal in the $B1$ structure is a superconductor with $T_c\sim 11.5$ K, while for substitutional $M\mathrm{C}_x\mathrm{N}_{1-x}$ alloys T_c is about 25 K.

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