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Electronic properties of transition-metal nitrides: The group-V and group-VI nitrides VN, NbN, TaN, CrN, MoN, and WN

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Motivated by the prediction that B1-structure MoN is a high-temperature superconductor, we present self-consistent augmented-plane-wave calculations of the electronic structure of the group-V and group-VI transition-metal nitrides VN, NbN, TaN, CrN, MoN, and WN. Comparisons of the energy bands, densities of states, and general bonding characteristics are made within this group, as well as with previously calculated transition-metal carbides. The calculated Stoner enhancement factor S for CrN indicates that the paramagnetic state is unstable with respect to ferromagnetism, consistent with the known antiferromagnetism in this compound. The calculated value of $S=2.15$ for MoN is not large enough to provide a serious impediment to superconductivity. The superconducting properties are evaluated within the Gaspari-Gyorffy theory for the electron-phonon coupling constant λ, calculated to be ~ 1.6 in MoN (about 60% larger than in NbN). The problem of stabilizing the metastable B1 structure over the thermodynamically more stable hexagonal MoN material is considered.

I. INTRODUCTION

The transition-metal carbides and nitrides are well known for possessing a number of extreme properties.[1] Their hardness, brittleness, and high melting points reflect unusual electronic bonding, and the high superconducting transition temperature T_c in several of these compounds, reaching[2] nearly 18 K in $NbC_{1-x}N_x$, indicates a strong electron-phonon interaction. The desire to understand such properties has stimulated a large number of theoretical investigations[3-9] of their electronic structure. These studies have uncovered an unusual mixture of covalent, metallic, and ionic contributions to bonding which must ultimately lie at the root of their unusual properties.

The group-IV and -V carbides and some of the nitrides in the rocksalt (B1) structure have been pursued vigorously, both experimentally and theoretically. In this paper we present corresponding results for the B1-structure group-VI nitrides, which are chemically much less stable, and compare them with the group-V nitrides. It seems that for both MoN and WN, the cubic B1 structure is energetically unfavorable, a hexagonal structure being preferred. However, theoretical studies of these two materials in the B1 structure are pertinent for two reasons. Firstly, early crystallographic studies,[10,11] of both NbN and TaN reported the stable stoichiometric phase of these metals to be hexagonal. Subsequent development of several new techniques have led to the preparation of cubic (B1 structure) samples at or near stoichiometry. Secondly, it has become increasingly commonplace recently to prepare reproducibly compounds in structures which are not the most stable ones, and indeed "nonequilibrium phase diagrams" have become an intense field of study. For these reasons we believe it to be entirely reasonable to investigate structural phases, viz., B1 MoN, which have not yet been fabricated in the laboratory.

The group-VI carbides and nitrides are unusual in a number of respects. CrN, which forms in the B1 structure,[1,10] is antiferromagnetic[12] with a Néel temperature of 297 K. The mononitrides (and monocarbides) of Mo and W, which form in (or near) the hexagonal WC structure, are interesting because of their superconducting behavior[7,13-16] as well as for their extreme hardness. MoN in its hexagonal form was first synthesized by Matthias and Hulm,[14] who reported $T_c=12$ K; values of T_c up to 14.8 K have been reported[16] since. Noting that most high-temperature superconductivity occurs in cubic compounds, it might be anticipated that, if MoN and/or WN can be stabilized in the B1 structure, their T_c values would be considerably higher. A prime example of the favorability of cubic structures for T_c is WC, where T_c in the B1 structure[17] is 10 K but the hexagonal form is not superconducting[14] above 1.28 K.

A theoretical argument which suggests that B1 MoN would have a high T_c results from applying the rigid-band model to the previously calculated[5] density of states (DOS) of NbN. Adding an extra electron moves the Fermi level E_F into a region with considerably higher DOS, which is directly correlated to T_c in this class of compounds. These arguments led us to calculate the electronic structure and T_c for B1 MoN. The results, published briefly elsewhere,[7] indicate that T_c(MoN) should be considerably higher than T_c(NbN) (=17 K) and might approach or exceed 30 K. Recently Zhao and He[18] have arrived at similar conclusions on purely empirical grounds.

The purpose of the present paper is to investigate in some detail the electronic structure of this class of compounds, with a view toward obtaining a more fundamental understanding of their remarkable properties, including their apparent metastability. The problem of fabricating MoN in the B1 phase is discussed in the final section of this paper.

II. CALCULATIONAL DETAILS

The electronic structure calculations were carried out using the self-consistent semirelativistic augmented-plane-wave method described previously.[3,4] The potential was taken to be of the muffin-tin (MT) form, which has been shown to work well in other B1 compounds, and the local-density exchange-correlation potential of either the $X\alpha$ or the Hedin-Lundqvist form was used. The lattice constants and MT radii of each compound are listed in Table I. The lattice constant of MoN given in this table was obtained in the following way. We first determined the lattice constant a of stoichiometric MoC ($a=4.343$ Å) by linear extrapolation from measured values[1,10,19] for $\mathrm{MoC}_{0.69}$ and $\mathrm{MoC}_{0.75}$, since a is reported to be linear in the concentration in this range. Then the lattice constant $a=4.250$ Å of stoichiometric MoN was obtained by assuming

$$a(\mathrm{MoC})-a(\mathrm{MoN})=a(\mathrm{NbC})-a(\mathrm{NbN})\ . \tag{1}$$

where $a(\mathrm{NbC})=4.47$ Å. The only reported experimental value[15] for "B1 MoN_x" is 4.16 Å but the N concentration in this sample was unknown.

Recently Klein *et al.*[20] and Williams *et al.*[20] reported theoretical values of 4.17 Å and 4.35 Å, respectively, obtained from total-energy calculations. Including the zero-point motion would raise these values by approximately 0.5%. Zhao and He[18] estimated $a=4.22$ Å for MoN based on empirical arguments. Therefore we are reasonably confident that the value of 4.25 Å we have used is correct to within about 1%.

Self-consistency of the band eigenvalues within ~2 mRy was achieved after about six iterations except for CrN, which required 18 iterations. The large number of iterations needed for CrN is due to the increased tendency toward fluctuations due to the very high DOS at the Fermi level. The final bands and wave functions were calculated at 20 $\vec{k}$ points in the irreducible zone and interpolated to the regular 89-point mesh (and in some cases to a 505-point mesh) using Boyer's[21] interpolation scheme. The total and partial DOS's were calculated using the standard tetrahedron method.[22] We also list in Table I the form of exchange correlation potential and type of radial equation (semirelativistic as devised by Harmon and Koelling,[23] or nonrelativistic) which were used in the calculations.

III. ELECTRONIC STRUCTURE RESULTS

A. General trends

In Figs. 1–3 the energy bands and DOS's of the B1 structure group-VI nitrides CrN (paramagnetic), MoN, and WN, respectively, are shown. The overall features are similar to those of previously published[4–9] carbides and nitrides. In Table II the values of characteristic band separations are given. We have selected for comparison the gap E_g between the N s band and the valence-band complex, the zone-center d-band splitting $\Delta E_d \equiv E(\Gamma_{12})-E(\Gamma_{25'})$, the metal d–Np splitting E_d-E_p [where $E_d \equiv \frac{2}{5}E(\Gamma_{12})+\frac{3}{5}E(\Gamma_{25'})$ and $E_p \equiv E(\Gamma_{15})$], and the N$p$–N$s$ splitting $E_p-E_s=E(\Gamma_{15})-E(\Gamma_1)$. The smooth trends which can be observed from Table II reflect first of all the broadening of the d states going down the columns V→Nb→Ta and Cr→Mo→W. As a result, the gap E_g decreases and the zone-center d splitting ΔE_d increases. The d bands are also broader in the group-V compounds than in the group-VI compounds, so both trends follow the pure metals in this respect. The p-s splitting E_p-E_s is essentially constant at 1.1 Ry, independent of the metal atom.

The quantity E_d-E_p, which is one measure of the relative positions of the metal d and N p, states, also increases smoothly in going down a column and is larger in the group-V compounds than in their group-VI counterparts. Although E_d-E_p varies from 0.03 Ry in CrN to 0.21 Ry in TaN, the large p–d hybridization mixes the bands so thoroughly that the total and partial DOS's (Figs. 1–3) appear very similar. The N p states also hybridize strong-

TABLE I. Calculational input to the augmented-plane-wave calculations. Lattice constant (a), metal atom muffin-tin radius (R_M), and nitrogen muffin-tin radius (R_N) are given in a.u. The exchange-correlation (XC) potential, of either Hedin-Lundqvist (HL) or $X\alpha$ form, and the use of semirelativistic (SR) or nonrelativistic (NR) radial equations, are indicated.

	a	R_M	R_N	Form of XC	Radial equation
CrN	7.8235	2.1829	1.7288	HL	SR
MoN	8.0314	2.2409	1.7748	HL	SR
WN	7.9369	2.2142	1.7537	HL	SR
VN	7.8232	2.0722	1.8394	$X\alpha$[a]	NR[b]
NbN	8.2730	2.3084	1.8282	$X\alpha$[a]	SR
TaN	8.3091	2.3181	1.8360	HL	SR

[a] $X\alpha$ coefficient taken from K. Schwarz, Phys. Rev. B 5, 2466 (1972).

[b] Self-consistent potential taken from K. Schwarz (unpublished).

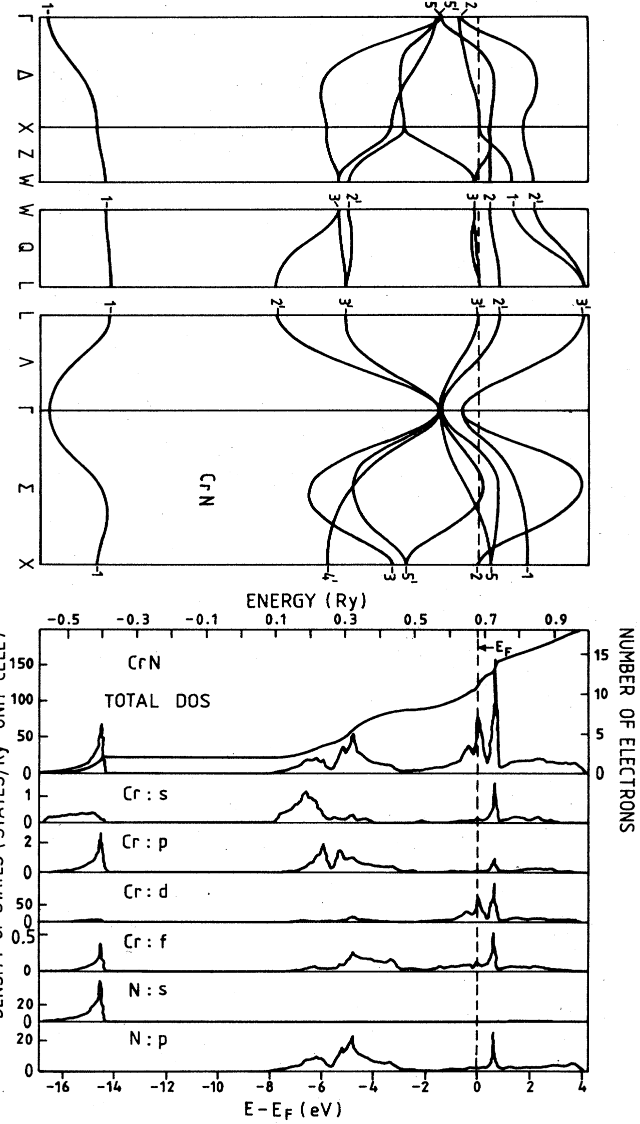

FIG. 1. Energy band structure and total and local densities of states for B1 CrN.

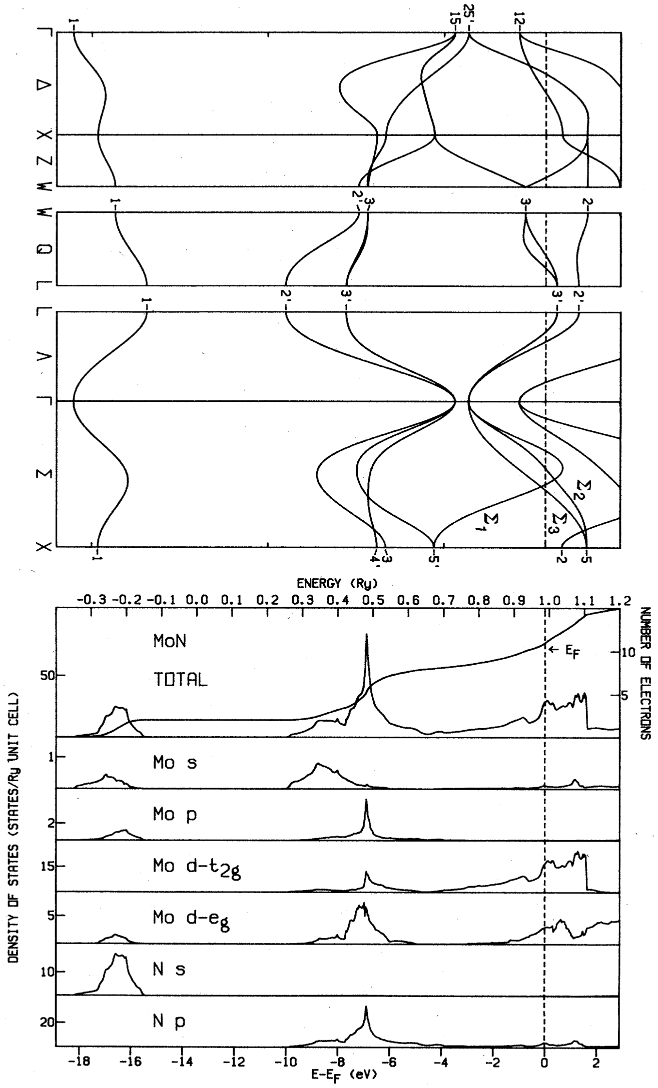

FIG. 2. As Fig. 1, for B1 MoN. In this case the Mo d density of states has been broken down into its e_g and t_{2g} components. The Σ_1, Σ_2, and Σ_3 bands are discussed in the text.

ly with the metal-atom s state. As a result of the highly diffuse nature of the metal s state, it also mixes with the N s state, resulting in a bandwidth of 0.20—0.25 Ry. In Table II we also present for comparison the characteristic widths for VC. It is interesting to note that $E_d - E_F < 0$ for VC, indicative of the stronger hybridization between metal and nonmetal states near E_F occurring for the carbides.

The DOS of the valence-band complex is characterized by two-high-density regions separated by a low-density region (sometimes designated as a bonding-antibonding "gap"). The lower, bonding states are of two types: a metal s—N p combination at the bottom, with a larger metal d—N p bonding combination just above. It is this strong hybridization, which places most of the occupied valence states 0.4—0.5 Ry below E_F, that is thought to be related to strong bonding properties of the related transition-metal carbides. The upper region of the valence-band complex, ranging from somewhat below E_F to roughly 0.5 Ry above E_F, is composed primarily of metal d states, but also contains a small N p component (typically 10—15 % at E_F) which can influence material properties to some extent (e.g., superconductivity, see Sec. III C). Blaha and Schwarz[24] and Trebin and Bross[25] recently have presented total and state charge density plots for Ti compounds, illustrating some aspects of the unusual bonding in these materials.

In Fig. 2 the Mo d DOS is broken down into its e_g and t_{2g} components. This decomposition illustrates that most of the d states which are occupied in MoN but unoccupied in NbN (which has $E_F \simeq 0.9$ Ry in Fig. 2 in a rigid band model) are t_{2g} states. The wave functions point in

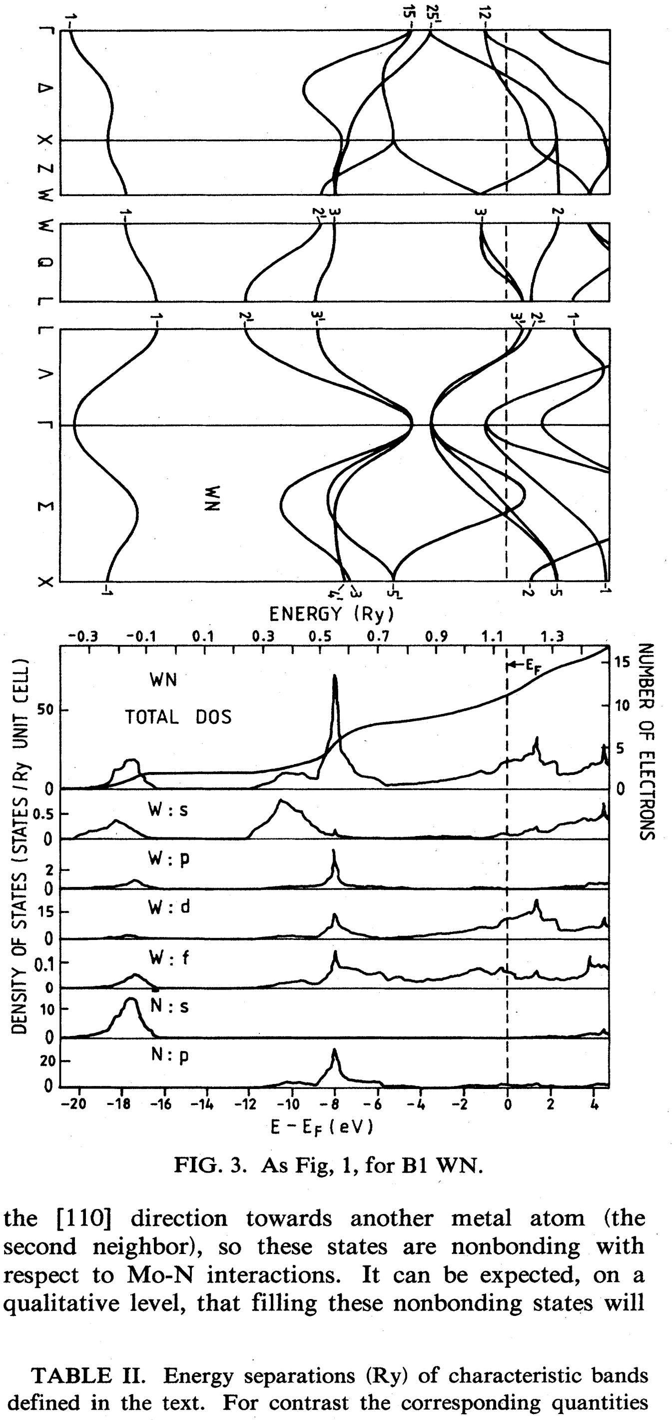

FIG. 3. As Fig, 1, for B1 WN.

the [110] direction towards another metal atom (the second neighbor), so these states are nonbonding with respect to Mo-N interactions. It can be expected, on a qualitative level, that filling these nonbonding states will not contribute added cohesion and may lead to a material which is less stable than is NbN.

As remarked previously, this study was motivated by the observation that a rigid-band model extrapolation based on NbN resulted in an estimated value of $N(E_F)$ appropriate to MoN which was 40% larger than in NbN. The actual band-structure calculation for MoN leads to an unexpected increase of 120%, so an investigation of the differences between MoN and NbN may be revealing. We fix the relative energy scales by aligning the Γ_{15} states, which also makes the Fermi levels coincide. We concentrate now on the bands connecting Γ and X along the Σ [110] direction (i.e., $\Gamma \rightarrow K \rightarrow X$) in Figs. 1–3. X_5, which lies above $\Gamma_{25'}$ (and above E_F), is more than 1 eV lower in MoN than in NbN, resulting in flatter Σ_2 and Σ_3 bands, which terminate at the X_5 level (see Fig. 2). In addition, the crossings of the Σ_1 band with the Σ_2 and Σ_3 bands occur near and on opposite sides of E_F. Off the Σ direction these become flattened anticrossings. All of these effects conspire to increase $N(E)$ for $E \approx E_F$ substantially above that predicted by the rigid-band picture, which takes no account of the p-d shift (Table II) of MoN relative to NbN. This points out that although the rigid-band model can be qualitatively suggestive, detailed self-consistent energy band calculations are needed for determining accurate quantitative results.

B. Magnetic susceptibility

In the mean-field Stoner theory the exchange-enhanced spin susceptibility at zero temperature is given by

$$\chi_{\rm sp}=\mu_B^2 N(E_F)/[1-I_F N(E_F)]\equiv\mu_B^2 N(E_F) S_F \ , \qquad (2)$$

where μ_B is the Bohr magneton and I_F is a generalized Stoner parameter, which can be evaluated from the paramagnetic band structure within the local density approximation.[26,27] The results are presented in Table III and $I_F N(E_F)$ is shown in Fig. 4(b).

Stoner theory predicts a ferromagnetic instability when $I_F N(E_F) \geq 1$. Except for CrN, the paramagnetic state is predicted to be the stable one. For VN the Stoner enhancement $S_F=3.87$ is larger than that reported ($S_F=2.9$) from the cluster calculations of Rietschel *et al.*,[28] due to our larger calculated value of $N(E_F)$. MoN, which has nearly the same calculated value of $N(E_F)$ as VN, has a 45% smaller enhancement due to the

TABLE II. Energy separations (Ry) of characteristic bands defined in the text. For contrast the corresponding quantities are presented for the B1 carbide VC.

	E_g	ΔE_d	E_d-E_p	E_p-E_s
(VC)	(0.21)	(0.07)	(−0.10)	(0.94)
VN	0.48	0.08	0.08	1.13
NbN	0.44	0.15	0.16	1.05
TaN	0.37	0.17	0.21	1.10
CrN	0.48	0.06	0.03	1.12
MoN	0.40	0.14	0.10	1.07
WN	0.31	0.19	0.14	1.17

TABLE III. Fermi-level density of states $N(E_F)$ (eV spin unit cell)$^{-1}$, generalized Stoner interaction constant I_F (eV), and Stoner enhancement $S_F=[1-I_F N(E_F)]^{-1}$ for transition-metal nitrides.

	$N(E_F)$	I_F	$I_F N(E_F)$	S_F
VN	1.12	0.66	0.74	3.87
NbN	0.47	0.40	0.19	1.24
TaN	0.43	0.33	0.14	1.16
CrN	3.05	0.79	2.41	−0.71
MoN	1.14	0.47	0.54	2.15
WN	0.65	0.41	0.27	1.37

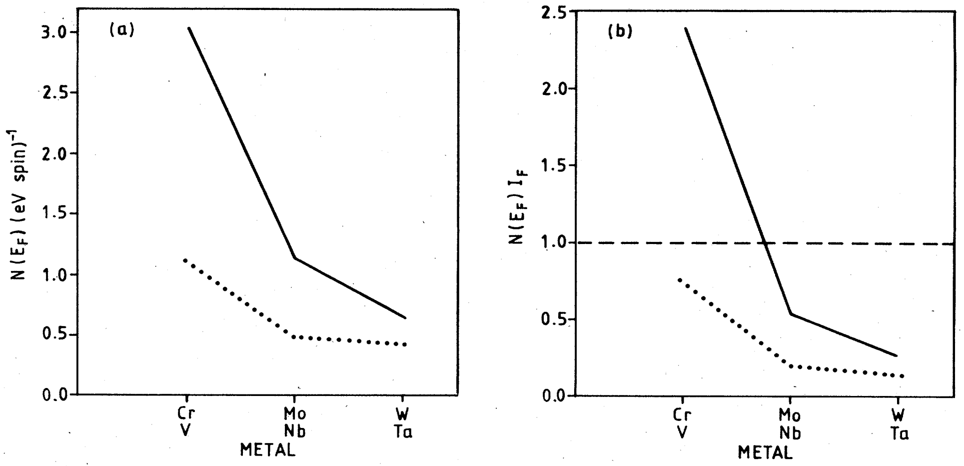

FIG. 4. Results for (a) $N(E_F)$ and (b) the product $N(E_F)I_F$, for group-V nitrides (dotted line) and group-VI nitrides (solid lines).

smaller exchange constant I_F. The decrease in I_F in the nitrides in going from $3d \rightarrow 4d \rightarrow 5d$ compounds reflects the same trend as was shown by Janak's calculations[26] for the elements. Aside from VN, and to a lesser extent MoN, these nitrides show moderate Stoner enhancements.

Our calculations clearly predict a magnetic instability in CrN, partly due to the large value of I_F but primarily as a result of the large value of $N(E_F)$. This result is consistent with experiment,[12] which finds CrN to be antiferromagnetic with a Cr moment of $2.41\mu_B$.

C. Superconducting transition temperature

The electron-ion interaction constant η has been calculated using the "rigid muffin-tin" approximation (RMTA) of Gaspari and Gyorffy:[29]

$$\eta_\alpha = N(E_F)\langle I^2\rangle_\alpha$$
$$= \frac{E_F}{\pi^2 N(E_F)} \sum_l 2(l+1)\sin^2(\delta^\alpha_{l+1}-\delta^\alpha_l)\frac{N^\alpha_l N^\alpha_{l+1}}{N^{(1)\alpha}_l N^{(1)\alpha}_{l+1}} \ . \tag{3}$$

In this expression δ^α_l are the scattering phase shifts at E_F for atom α and angular momentum l, $N^{(1)\alpha}_l$ are the single scatterer densities of states defined in Ref. 29, and N^α_l are the site-angular-momentum densities of states at E_F.

The quantity η_α is plotted in Fig. 5(a) for both the group-V and -VI nitrides. From Figs. 4 and 5 we note the following.

(i) As was found for other carbides and nitrides,[4-7] the metal component η_M, which has its main contribution from the metal d states at E_F, is much larger than the nitrogen component η_N, which is dominated by the nitrogen p states at E_F.

(ii) η_M and η_N show rather small variations within the group-V nitrides. However, for the group-VI nitrides they show a pronounced maximum at MoN which obviously suggests possibilities for high T_c.

(iii) Especially in the group-VI nitrides, η_M and η_N do not follow the variation of $N(E_F)$. Indeed $N(E_F)$ of CrN is larger than that of MoN by almost a factor of 3, while η_M for MoN is approximately 1.5 times the η_M of CrN. This indicates the importance of the electron ion scattering matrix element $\langle I^2_{e\text{-ph}}\rangle$ which is obviously very small for CrN. In this respect the late $3d$ elements are similar to $4f$ and $5f$ electron systems, which do not couple strongly to itinerant states and therefore result in small electron-phonon coupling[30] despite large values of $N(E_F)$.

(iv) The $3d$ metal (V or Cr) nitrides have considerably higher values of $N(E_F)$, conducive to a magnetic instability, but rather smaller electron-ion matrix elements than do their $4d$- and $5d$-metal counterparts. This behavior also is similar to that found for the pure elements.[31]

A proper calculation of T_c requires knowledge of the phonon spectrum, which is not known for any of the group-VI nitrides. Therefore we apply the same approximate theory which has been found to work well in previous calculations[4-7,32] for nitrides and carbides. This approach is expected to *reproduce trends correctly* and to give realistic differences in T_c between related compounds as long as their phonon spectra are similar. The present calculation of T_c proceeds as follows. The electron-phonon coupling constant λ is given in terms of metal and nitrogen sites by[4,32]

$$\lambda = \frac{\eta_M}{M_M\langle\omega^2_M\rangle} + \frac{\eta_N}{M_N\langle\omega^2_N\rangle} \equiv \lambda_M + \lambda_N \ . \tag{4}$$

Our estimates of $M_M\langle\omega^2_M\rangle$ and $M_N\langle\omega^2_N\rangle$ are based on the neutron scattering data analysis of Weber[33] and Feldman,[34] and measurements of the Debye temperatures for the $NbC_{1-x}N_x$ system.[35] These data measure only the phonon spectrum, so our estimates of $M_\alpha\langle\omega^2_\alpha\rangle$ do *not* account for a possible frequency dependence of the electron-phonon coupling. These estimates were made in the following way. From the above data[33,34] we have a reliable evaluation of the $M_\alpha\langle\omega^2_\alpha\rangle$ for the Nb and C sites in $NbC_{1.0}$. Using the Debye temperatures[35] given for $NbC_{1-x}N_x$ we deduced, by linear interpolation and scaling of the nonmetal atom masses, the $M_\alpha\langle\omega^2_\alpha\rangle$ of Nb and N in $NbN_{1.0}$. Similarly, using the measured Debye temperatures[1,10] of VN, CrN, and TaN, we again interpolated linearly, taking into account the different masses of the

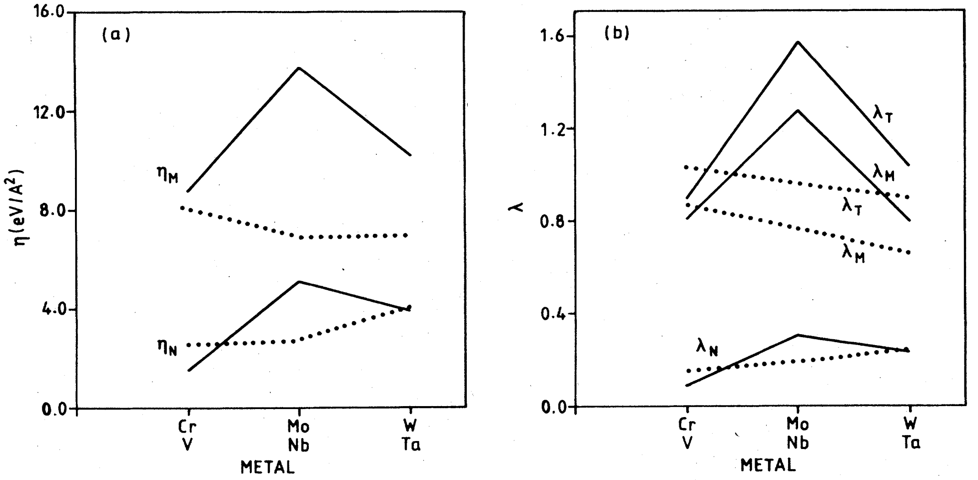

FIG. 5. Calculated values of (a) η_M and η_N and (b) coupling strengths λ_M and λ_N and their sum λ_T, for the group-V nitrides (dotted lines) and the group-VI nitrides (solid lines).

metal sites. This prescription probably provides a conservative estimate of the increase in λ in MoN over that of NbN, since simply taking $M_\alpha\langle\omega_\alpha^2\rangle$ values from NbN (a reasonable procedure in the absence of any experimental information) would have led to a 15% larger value of λ.

The resulting λ's, shown in Fig. 5(b), display very similar variation to that of the η's. The distinct maximum at MoN in fact becomes somewhat more pronounced. T_c is given by the modified McMillan equation established by Allen and Dynes:[36]

$$T_c=\frac{\omega_{\log}}{1.20}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*-0.62\lambda\mu^*}\right], \tag{5}$$

with $\omega_{\log}$ determined as described in Ref. 4. We have used the following modification[5] of the Bennemann-Garland[37] empirical formula for the Coulomb pseudopotential μ^*:

$$\mu^*=0.20N(E_F)/[1+N(E_F)] \tag{6}$$

with $N(E_F)$ in units of states for both spins/(eV unit cell). This introduces via $N(E_F)$ a small variation of μ^* which results in a *reduction* of T_c with increasing $N(E_F)$. Our results for the intermediate electronic quantities and for λ_α and λ are given in Table IV. The calculated values of λ for these nitrides are within 10% of unity except for MoN, for which $\lambda=1.58$.

In very-high-$N(E_F)$ materials (usually $3d$ systems), spin fluctuations (SF) are sometimes invoked to reconcile severe theoretical overestimates with reality. The SF theory of Berk and Schrieffer,[38] which they suggested would be applicable to nearly ferromagnetic metals with $S_F>5$, is the only one available. Since S_F for MoN is just over 2 (Table III), we see no reason to expect SF's to interfere with superconductivity. In fact there is no indication of appreciable SF effects in any compound based on a $4d$ metal in the middle of the transition series.

Rietschel *et al.*[28] have applied this SF theory to VN. Their method of calculation of T_c, which differs in many ways from ours, leads to $\lambda=1.54$ and $T_c=32.3$ K, both substantially larger than our values (Table V). Within the SF theory a paramagnon mass enhancement $\lambda_{\text{sp}}=0.54$ is required to bring their theoretical value into agreement with experiment. For our calculation, $\lambda_{\text{sp}}\simeq 0.15$ will reproduce the experimental value. However, there is evidence that the RMTA overestimates λ and, hence, T_c in $3d$ metals,[30] so even this reduced value of λ_{sp} may be an overestimate. Since the corresponding changes in T_c for the other nitrides would be much smaller, we have not ap-

TABLE IV. Fermi-level density of states (eV spin unit cell)$^{-1}$, Hopfield-McMillan constant η_α (eV/Å^2), electron-ion scattering matrix element $\langle I^2_{e\text{-ph}}\rangle_\alpha$ (eV^2/Å^2), and electron-phonon coupling constant λ_α for each atom α (in subscript, M represents metal atom, N represents nitrogen). Coulomb pseudopotential μ^* and total electron-phonon coupling constant λ_{tot} used in the calculation of T_c are also shown.

	$N(E_F)$	η_M	η_N	$\langle I^2\rangle_M$	$\langle I^2\rangle_N$	μ^*	λ_M	λ_N	λ_{tot}
VN	1.12	8.05	2.5	7.2	2.3	0.14	0.87	0.15	1.02
NbN	0.47	7.0	3.2	14.9	6.8	0.10	0.77	0.19	0.96
TaN	0.43	7.0	4.1	16.3	9.5	0.09	0.66	0.24	0.90
CrN	3.05	8.75	1.5	2.9	0.5	0.17	0.81	0.09	0.90
MoN	1.14	13.8	5.1	12.1	4.5	0.14	1.28	0.30	1.58
WN	0.65	10.15	3.9	15.7	6.0	0.11	0.80	0.23	1.03

TABLE V. Calculated electron-phonon coupling constant λ, and theoretical and experimental values of the linear specific heat coefficient γ (mJ/mol K^2) and superconducting transition temperature T_c. Experimental values (in many cases from substoichiometric samples) are taken from Toth (Ref. 1) and from Refs. 52 and 53.

	λ	γ_{theor}	γ_{expt}	$T_{c,\text{theor}}$	$T_{c,\text{expt}}$
VN	1.02	9.1	8.6	19.7	9.25
NbN	0.96	4.3	4.08—4.56	17.1[a]	17.0
TaN	0.90	3.8		14.6	8.9
CrN	0.90	26.8	(magnetic)	12.4	(magnetic)
MoN	1.58	13.6		29.4	
WN	1.03	6.1		15.8	

[a] This value of T_c differs slightly from that published earlier ($T_c = 16$ K, Refs. 5 and 7) due to the use of the Hedin-Lundqvist exchange-correlation potential rather than the $X\alpha$ form in the band calculation.

plied the SF theory in the results presented here.

We have also used our calculated mass enhancement factor $(1+\lambda)$ together with $N(E_F)$ to obtain a value for the linear specific heat coefficient γ. These γ values and the calculated values of T_c are compared to the available experimental ones[1,10] in Table V for the group-V and -VI nitrides. For γ only values for VN and NbN are available, and the agreement is excellent. The 5% overestimate by our calculations is well within the overall accuracy of the theory. However, the data may be appropriate for slightly substoichiometric samples which would probably underestimate the value of γ for the stoichiometric nitrides.

The remarkable aspect of these calculations is the value of $T_c = 29$ K predicted for MoN. This is 25% higher than the highest known T_c of 23 K for Nb_3Ge. It should be noted that our method of calculation has been aimed at *reproducing trends* for T_c in these nitrides within a given row of the Periodic Table. (Absolute values of T_c may be wrong in individual calculations by $\sim 50\%$ due to lack of knowledge of μ^*, phonon moments, and the use of RMTA. Also, trends involving $3d$ elements are suspect, due to possible magnetic correlations or to shortcomings of the RMTA in these materials [Klein and Pickett (Ref. 30)].) For NbC and NbN, for example, the trend in T_c is predicted correctly.[5] Moreover, our theory is "normalized" correctly at NbN (see Table V). Furthermore, the use of $\mu^*[N(E_F)]$ from Eq. (6) takes into account an increased effect of Coulomb repulsion between paired electrons for systems with large $N(E_F)$ and leads to a more pessimistic prediction for T_c (by 4 K for MoN) than would result from the commonly made constant-μ^* approximation. Finally, we have not taken into account the increased electron-phonon coupling from phonon softening which is likely to accompany the large value of $N(E_F)$. Thus we expect that $T_c = 29$ K is a somewhat pessimistic prediction of the superconducting transition temperature in *ordered stoichiometric* cubic MoN.

IV. STABILIZATION OF METASTABLE PHASES

A. Methods

The results presented in Sec. III support the earlier claim that stoichiometric B1 MoN would be a high-temperature superconductor, quite possibly higher than all presently known superconductors. It is also likely that B1 MoN would possess other extreme properties as well. The problem becomes one of finding a method of stabilizing the B1 phase.

The equilibrium phase diagram of the Mo-N system has been discussed most recently by Jahn and Ettmayer.[39] Below 35 at. % N, several mixed phases (bcc α, tetragonal β, fcc γ) of "Mo_2N" (actually $Mo_2N_{1\pm x}$) occur. The B1 phase of MoN we are considering is equivalent to the fcc γ phase with identical Mo and N concentrations. At precisely 50 at. % the stoichiometric line compound δ-MoN occurs. δ-MoN was obtained by passing ammonia, which has a very high nitrogen potential, over Mo powder heated to 700—1000 °C. Schönberg[11] determined the structure of δ-MoN to be hexagonal ($P6_3mmc$). Troitskaya and Pinsker,[40] studying samples of MoN obtained by nitriding vapor-deposited Mo films with flowing ammonia, identified two similar forms, δ'-MoN and δ''-MoN. These are also hexagonal and differ primarily in the positions of the N atoms, which in any case are difficult to determine unambiguously due to their small contribution to the diffraction intensities.

Since the hexagonal phase (δ or δ', δ'') of MoN is the thermodynamically stable one for the stoichiometric composition, one must consider nonequilibrium growth techniques in the hope that the B1 structure can be stabilized in some fashion. An obvious possibility is sputtering Mo in N_2, CN, or ammonia vapor, not only because many metastable phases have resulted from this type of sputtering process but also because this has become a widespread technique[2,41] in making the structurally identical and chemically related alloys $NbC_{1-x}N_x$. A related technique, which is amenable to careful control of the deposition parameters, is electron-beam (co-) evaporation.[42] Vapor deposition, including organometallic transport or ion implantation of N into Mo films followed by (standard or laser) annealing are other possibilities. Finally, one may try high-temperature and/or high-pressure treatment of δ-MoN, either by laboratory methods or by shock compression.

This latter possibility seems to be a promising possibility, particularly since a high-T_c $A15$ phase of Nb_3Si has been obtained by shock compression by Olinger and Newkirk.[43] Shock compression requires obtaining a bulk sample of stoichiometric MoN (approximately cubic centimeter quantities rather than the thin wires or thin films studies up to the present) and subjecting it to brief pressures of several megabars by explosive techniques. The (existing) structure of δ-MoN and the (desired) structure of B1 MoN appear to be favorable for shock compression (a nondiffusive process) to "work."[44] First, we note that the molecular volume of δ-MoN corresponds to a cubic lattice constant of 4.30 Å, so the equilibrium volume of the cubic structure is smaller than that of the hexagonal structure. Second, it takes only correlated movements of (111) planes of Mo atoms by a fraction of the lattice spacing to convert the hexagonal arrangement of Mo in δ-MoN to the fcc arrangement in B1 MoN. The lighter N atoms would also have no difficulty in attaining the desired positions. A necessary condition for this procedure to succeed is that the B1 structure becomes more stable than the hexagonal ones at high pressure. We are presently investigating this question by carrying out total energy versus volume calculations[20] for both structures. These calculations will also allow us to predict the critical pressure for transformation.

Variations on the sputtering and electron-beam-evaporation methods also seem promising. One approach is to induce the stabilization of MoN by growing epitaxially on a related compound; NbN, CrN, and $NbC_{1-x}N_x$ are possibilities and techniques for making films of the Nb-based alloys are known. Approaching MoN through the pseudoquaternary system $Nb_{1-y}Mo_yC_{1-x}N_x$ has also been considered.[41] There is also the possibility of applying large effective pressures, which may be either positive or negative, by growing sandwich structures or multilayers of the form NbN-MoN-NbN or CrN-MoN-CrN. A structure of the latter type would be interesting in its own right, for observing the interplay between superconductivity and magnetism.

B. Survey of past experimental work on MoN

As mentioned previously, Saur *et al.*[15] reported a small amount of a second phase, referred to as B1 MoN, from samples prepared by passing ammonia over Mo wires 0.5 mm in diameter heated to 750–950 °C. The reported lattice constant of 4.16 Å is significantly smaller than our empirical estimate of 4.25 Å as well as the value of 4.22 Å estimated by Zhao and He.[18] Both the small lattice parameter and the method of preparation indicate that this second-phase material is the thermodynamically stable γ-phase MoN_x with $x \approx 0.7$. The possible role of hydrogen in the formation of this material is unknown but should not be overlooked.

Ion implantation has been used by various groups to synthesize MoN_x samples. Using high-energy ions, Belli *et al.*[45] found γ-phase material of unknown N concentration with $a = 4.16$–4.17 Å, while Afanseev *et al.*[46] found no γ-phase material, using somewhat lower energy N ions. Bykov *et al.*[47] report the formation of γ-MoN_x with $a = 4.22$ Å with even lower energy N ions. These findings indicate a strong sensitivity of MoN_x formation to ion energy as well as fluence. More recently Linker *et al.*[48] have used multiple ion energies and fluences to produce more homogeneous films with fcc lattice parameter $a = 4.212$ Å (discussed further below).

Films of Mo have been nitrided by Kim *et al.*[49] by heating in ammonia and forming gas. By varying the experimental conditions it was possible to form nearly 100% δ-MoN films or to produce multiphase (including γ-MoN films. Ettmayer *et al.*[50] have studied the Cr-Mo-N phase diagram by nitriding the metal powders at high temperature and at pressures up to 300 bars. They found a complete series of solid solutions of $(Cr_{1-y}Mo_y)N_x$; however, whereas $x = 1$ may be achieved at the Cr-rich end ($y = 0$), substitution of Mo for Cr results in nonstoichiometric ($x < 1$) material, in agreement with the phase diagram at the Mo-rich end. Unfortunately these studies, like most of those above, were concerned with little more than structural information and also did not address the question of the effect of other elements (particularly O and H) on material formation.

By using ion implantation and reactive sputtering Linker, Smithey, and Meyer[48] (LSM) have produced γ-MoN_x films in the range $x \le 1.1$. The lattice constant measured for $x = 1.0$, $a_0 = 4.212$ Å, indicates substantially more nitrogen than in previous work. The measured $T_c \sim 3$ K does not necessarily contradict our calculated value because, as we discuss below, these films may differ considerably from ordered MoN. The films have very large residual resistivities and residual resistivity ratios of 1 or less, apparently due to texture in the films, so it is not possible to use the resistivity to estimate the amount of structural disorder in these films. The x-ray diffraction studies of LSM indicate a well-developed *average* B1 lattice, but the texture of the films prohibits an analysis of the intensities which would establish the integrity of the individual sublattices in the B1 structure. Thus a *well-ordered* B1 lattice has *not* been established for these films.

Considering the metastability (at best) of the ordered B1 structure for MoN, and noting the strong tendency of transition metal carbonitrides to form vacancies on the nonmetal sublattice, it is likely that the nonmetal sublattice of the LSM films contains a substantial fraction of vacancies. As the fraction x of N is increased, nitrogen atoms may replace Mo atoms on the Mo sublattice, or alternatively, vacancies may be introduced on the Mo sublattice. NbO, for example, which contains the same number of valence electrons as MoN, forms a stoichiometric compound which may be regarded as an ordered array of 25% vacancies on *both* sublattices of the B1 structure, and is not superconducting above ~ 1 K. Either of these possibilities is consistent with the smooth behavior of the lattice constant and of T_c in the LSM MoN films in the region $x \approx 1.0$, which would *not* be expected if vacancies on the N sublattice were being filled for $x < 1.0$ and interstitials being created for $x > 1.0$. Moreover, the observed *decrease* in T_c with increasing x which was found by LSM is contrary to the behavior of other carbonitrides where increasing x does fill vacancies and increase T_c. The decrease in T_c, however, is consistent with the expected trend if the integrity of the Mo sublattice is being degraded. Data on other carbonitrides suggest that a metal sublattice of high integrity is more important for high T_c than stoichiometry if the latter comes at the expense of the former. Theoretical studies of the effects of disorder on the properties of MoN are planned to be published elsewhere.[51]

Note added in proof. T_c values exceeding 6 R in Mo-rich $Mo_yNb_{1-y}(N_xC_{1-x})_z$ thin films have been reported recently by S. A. Wolf, S. B. Qadri, K. E. Kihlstrom, R. M. Simon, W. W. Fuller, D. Van Vechten, E. F. Skelton, and D. U. Gubser [IEEE Trans. Magn. (to be published)].

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