

Effects of disorder on high-temperature superconductivity in cubic MoN

D. A. Papaconstantopoulos and W. E. Pickett
 Naval Research Laboratory, Washington, D.C. 20375-5000
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Three types of calculations have been used to help us understand the effects of disorder, alloying, and nonstoichiometry on the superconducting transition temperature T_c of MoN, predicted to have $T_c = 29$ K in the ideal $B1$ structure. (1) Simple disorder broadening indicates a strong lowering of T_c which, however, does not account for the very low T_c 's measured in MoN_x thin films. (2) Rigid-band calculations of the alloy system $\text{Nb}_{1-y}\text{Mo}_y\text{N}_{1.0}$ reproduce the measured trend in T_c for $y \leq 0.5$. (3) Taking explicit account of metal t_{2g} - Np bonding in a coherent-potential-approximation model of MoN_x leads to a semiquantitative understanding of the low measured T_c values in films in terms of N vacancies, despite the nominal stoichiometry in some of the films.

I. INTRODUCTION

In recent publications¹⁻³ it has been proposed that on the basis of energy-band-structure calculations the compound MoN, in the NaCl structure, is predicted to have a superconducting transition temperature $T_c \sim 29$ K. These calculations correspond strictly only to the ordered stoichiometric case. It could be argued that the above prediction is not realistic for a high- T_c transition-metal nitride because this class of compounds tends to form with vacancies on the nitrogen sublattice. Moreover, Linker *et al.*⁴ have fabricated nominally stoichiometric but not highly ordered MoN in the NaCl structure, which displays a value of T_c which is an order of magnitude below the predicted value. Although recent experimental studies of the Mo-Nb-N-C system by Wolf *et al.*⁵ have shown a trend of increasing T_c with increasing Mo content, they have not produced the predicted high T_c for the MoN end.

To check the effects of disorder, alloying, and nonstoichiometry in this system we have (a) calculated the effects of disorder on the density of states (DOS) of the stoichiometric MoN using the electron-lifetime model (ELM),⁶⁻⁸ (b) applied the rigid-band model on the band structures of NbN and MoN to estimate the electron-phonon interaction and T_c for the alloy system $\text{Nb}_{1-y}\text{Mo}_y\text{N}_{1.0}$, and (c) used the tight-binding coherent-potential-approximation (CPA) method⁹ to examine the effect of nitrogen vacancies.

II. ELECTRON-LIFETIME MODEL

The ELM assumes that defects simply broaden the DOS via the electron relaxation time, τ , which decreases with disorder. One then takes into account disorder effects by the following convolution of the DOS, $N(E', \Gamma=0)$:

$$N(E, \Gamma) = \int S(E, E', \Gamma) N(E', \Gamma=0) dE', \quad (1)$$

where $S(E, E', \Gamma)$ is a broadening function which depends on the electron damping $\Gamma = \hbar/\tau$. In the present calculation $S(E, E', \Gamma)$ is a Lorentzian whose half-width Γ is re-

lated to the infrared plasma energy Ω_p and the residual resistivity ρ_0 arising from disorder by the formula

$$\Gamma = 1.341 \times 10^4 \Omega_p^2 \rho_0, \quad (2)$$

where Ω_p is expressed in eV and ρ_0 in $\mu\Omega$ cm. The physical interpretation of this relation is discussed in Ref. 7.

A relation analogous to Eq. (1) was applied to broaden our calculated Ω_p^2 to obtain $\Omega_p^2(\Gamma)$, which was substituted into Eq. (2) to obtain the corresponding values of ρ_0 . In order to relate $N(E_F)$ and $\Omega_p(E_F)$ to the experimental ρ_{expt} we have made use of the fact that high- T_c metals display a temperature-dependent resistivity which is well described¹⁰ by the parallel resistor formula

$$\frac{1}{\rho_{\text{expt}}} = \frac{1}{\rho_0} + \frac{1}{\bar{\rho}}. \quad (3)$$

We use the canonical value¹⁰ of $\bar{\rho} = 150 \mu\Omega$ cm.

The results for $N(E_F, \Gamma)$ are displayed in Fig. 1. We note that for an amount of disorder corresponding to $\rho_{\text{expt}} = 32 \mu\Omega$ cm ($\rho_0 = 40 \mu\Omega$ cm) $N(E_F, \Gamma)$ drops from a value of 15.5 states/Ry spin (see Table I and Ref. 3) at

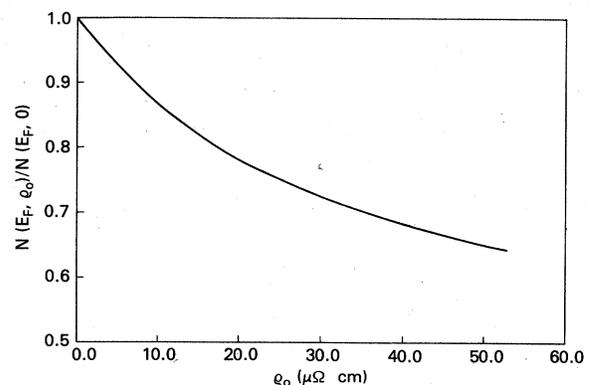


FIG. 1. Ratio of the Fermi-level density of states in disordered MoN to that of ideal $B1$ MoN, inferred from the electron-lifetime model vs the experimental residual resistivity ρ_0 .

TABLE I. Quantities related to the superconducting transition temperature T_c for the $\text{Nb}_{1-y}\text{Mo}_y\text{N}_{1.0}$ system, based on a rigid-band model from each end. The units are $N(E_F)$ (Ry spin-cell) $^{-1}$, η (eV/Å 2), λ and μ^* (dimensionless), ω_{\log} , and T_c (K).

y	$N(E_F)$	η_M	η_N	λ_M	λ_N	λ_{tot}	μ^*	ω_{\log}	T_c
Rigid band from NbN									
0.0	6.43	6.98	3.18	0.77	0.19	0.96	0.098	258	17.1
0.1	6.70	6.81	2.80	0.74	0.17	0.91	0.099	254	15.1
0.2	6.71	6.67	2.66	0.71	0.16	0.87	0.099	256	14.1
0.3	6.13	5.86	2.51	0.61	0.15	0.76	0.095	263	11.6
0.4	6.17	5.67	2.52	0.58	0.15	0.73	0.095	269	10.8
0.5	6.45	5.68	2.65	0.57	0.16	0.73	0.097	275	10.8
Rigid band from MoN									
0.5	7.67	7.00	2.70	0.71	0.16	0.87	0.106	263	13.9
0.6	8.66	7.81	3.13	0.77	0.19	0.96	0.112	268	16.5
0.7	10.00	9.15	3.67	0.89	0.22	1.11	0.119	271	20.3
0.8	12.36	10.30	3.49	0.99	0.21	1.20	0.129	264	20.9
0.9	14.45	12.99	4.57	1.22	0.27	1.49	0.136	269	27.4
1.0	15.50	13.84	5.05	1.28	0.30	1.58	0.139	276	29.4

$\rho_{\text{expt}}=0$, to a value of 10.3 states/Ry spin. Although this is a significant lowering of $N(E_F, \Gamma)$ we note that this is still a rather high DOS at E_F . For comparison we mention here that NbN, a superconductor with $T_c \approx 17$ K, has $N(E_F, 0)=6.43$ states/Ry spin (see Ref. 3). Therefore, we conclude that this unspecified form of disorder which serves only to broaden $N(E)$ will lower T_c from our suggested value for stoichiometric MoN. However, up to rather high levels of disorder it still gives a T_c higher than that of NbN.

III. RIGID-BAND MODEL FOR $\text{Nb}_{1-y}\text{Mo}_y\text{N}_{1.0}$

In an earlier publication¹¹ one of us applied the rigid-band approximation (RBA) on the band structures of NbC and NbN to evaluate the electron-ion interaction constant η and T_c for the system of Nb-C-N. These calculations reproduced very well the overall variation of T_c shown in the experiments. In a similar manner we used here the band-structure results for NbN and MoN to obtain partial DOS, N_i , and scattering phase shifts, δ_i , for the alloy $\text{Nb}_{1-y}\text{Mo}_y\text{N}_{1.0}$ needed in the determination of η by the theory of Gaspari and Gyorffy.¹² In our scheme, in the range $0 < y < 0.5$, we used the N_i 's and δ_i 's from the NbN band structure while in the range $0.5 \leq y < 1.0$ we used the corresponding quantities from the MoN band structure.

Our results show that $\eta_{\text{Mo(Nb)}}$ is roughly a factor of ~ 2.5 larger than η_N through the whole range of y . The value of η_N is $3.2 \text{ eV}/\text{Å}^2$ at the NbN end ($y=0$), decreases to $2.5 \text{ eV}/\text{Å}^2$ at $y=0.3-0.4$, and then increases monotonically to $5.1 \text{ eV}/\text{Å}^2$ at $y=1.0$. The value of $\eta_{\text{Mo(Nb)}}$ is $7.0 \text{ eV}/\text{Å}^2$ for $y=0$, decreases to $5.7 \text{ eV}/\text{Å}^2$ at $y=0.45$, and then increases to $13.8 \text{ eV}/\text{Å}^2$ at the MoN end ($y=1.0$). To calculate the electron-phonon coupling constant λ we have used neutron-scattering data and Debye-temperature measurements of the $\text{NbC}_{1-x}\text{N}_x$ sys-

tem as discussed in Ref. 3. We then employ the Allen-Dynes¹³ equation to calculate T_c with a DOS dependent μ^* given by a modified¹¹ Bennemann-Garland¹⁴ formula. Our results for the intermediate quantities and T_c are displayed in Table I. A plot of T_c as a function of Mo content is shown in Fig. 2. We note that T_c follows the variation of η or λ , i.e., it decreases from 17 K at the NbN end, reaches a minimum of 11 K at about $y=0.4$, and increases to 29 K at the MoN end. Recent measurements by Wolf *et al.*⁵ show a decrease of T_c with increasing y in agreement with that portion of the graph shown in Fig. 2. The calculated increase of T_c for the Mo-rich end has not been observed due to experimental difficulties in retaining a stoichiometric and ordered B1 structure for high-Mo concentrations.

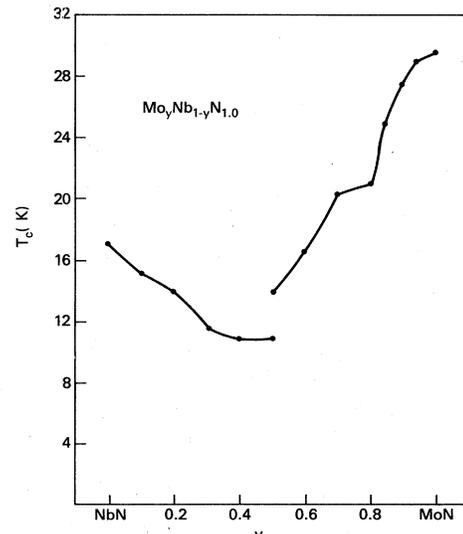


FIG. 2. Superconducting transition temperature T_c of $\text{Nb}_{1-y}\text{Mo}_y\text{N}$ alloys, based on a rigid-band model on the end points NbN and MoN.

IV. CPA CALCULATIONS FOR MoN_x

In Sec. II an unspecified disorder broadening was applied to the density of states of MoN . In this section we present results of a calculation performed utilizing the CPA to study the effects on the electronic structure of vacancies on the nitrogen sublattice in MoN . Our model assumes that the metal sublattice remains unchanged while the nitrogen sublattice contains vacancies at random. The tight-binding CPA theory that we used here originates from the work of Faulkner⁹ on PdH which was previously extended¹⁵ to include both s and p orbitals in the basis set of the vacancy atom. This involves a Slater-Koster tight-binding fit to the MoN energy bands and subsequent solution of the CPA condition for zero-average scattering from which the nonmetal sublattice self-energies Σ_s and Σ_p are determined. The quantities Σ_s and Σ_p are then used to calculate an effective Green's function from which the DOS are found.

We performed these calculations for nitrogen concentrations $1.0 > x \geq 0.5$ in steps of 0.1. In Fig. 3 we show

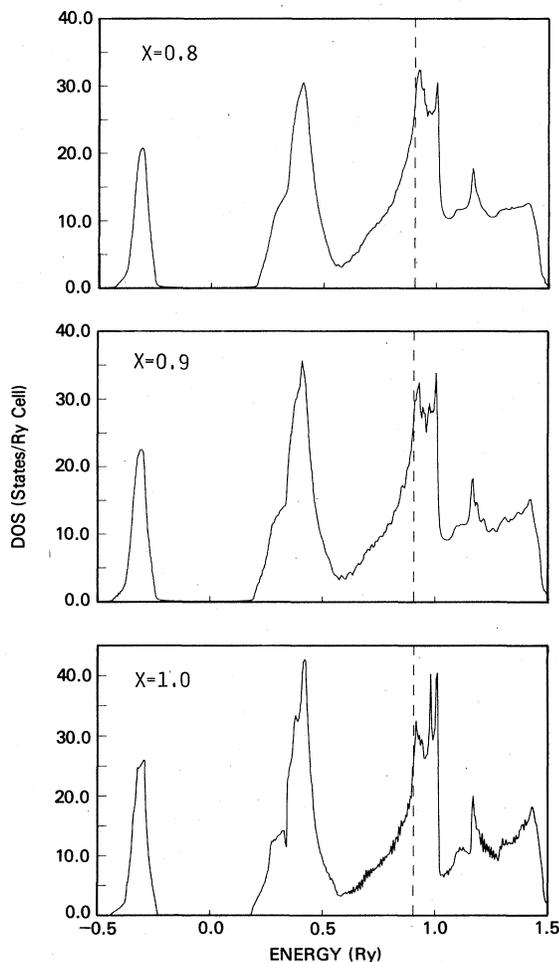


FIG. 3. Total density of states of MoN_x for the three nitrogen concentrations $x=0.8, 0.9,$ and 1.0 , based on the tight-binding CPA model.

the DOS for $x=0.9$ and 0.8 together with the stoichiometric case $x=1.0$. We note from Fig. 3 that the main characteristics of the stoichiometric MoN DOS are preserved upon the creation of vacancies. That is, we have a low-lying peak at about -0.3 Ry, due to the nitrogen s states, then a broader peak at about 0.4 Ry which corresponds to a mixture of Mo d states and N p states, and near the Fermi level another broad peak containing predominantly Mo states. The value of $N(E_F)$ remains within 1–2% of the stoichiometric value and the value of E_F changes by no more than ± 1 mRy as a function of x . This is different from the situation reported in Ref. 15 for NbC where E_F increases with decreasing x by approximately 20 mRy per $\Delta x=0.1$. We believe that this different behavior of E_F with x between MoN and the carbides is due to the fact that around E_F the p -C electrons experience a much stronger hybridization with the d electrons in the carbides than do the p -N electrons in the nitrides. The much larger value of $N(E_F)$ in MoN also serves to “pin” the Fermi level to some degree.

To quantify the variation of η with the amount of vacancies we note first that according to the earlier analysis of the bonding characteristics of transition-metal carbides,¹⁵ the metal-to-carbon charge transfer comes primarily from the metal t_{2g} states to the carbon p states. An examination of the integrated components of the DOS supports the same conclusion for MoN . Therefore, the concentration dependence of η will be dominated by that of the N p and Mo t_{2g} DOS.

One would like to have a quantitative theoretical description of the change in T_c due to vacancies on the nonmetal sublattice. Unfortunately, there is no viable microscopic theory for the electron-phonon interaction λ for such systems. The theory of Gaspari and Gyorffy (GG),¹² which makes the rigid muffin-tin approximation, has been applied widely and successfully in high-symmetry transition-metal-based compounds. However, this theory becomes much more approximate when applied to systems such as MoN_x , partially due to Mo atoms adjacent to vacancies (six Mo atoms for each vacancy) acquiring a much lower symmetry than cubic, and perhaps differing greatly in their scattering properties from an average-lattice CPA “atom.” In addition, the tight-binding CPA does not provide the changes in phase shifts which are needed in the GG theory. Ignoring changes in phase shifts and estimating from the calculated CPA local DOS, the GG theory applied directly to MoN_x would lead to only a small decrease in λ for $x \approx 0.5$. However, the strong decrease in T_c in both NbC and NbN and the disappearance of phonon anomalies¹⁶ in NbC , as x decreases, both indicate a large reduction in electron-phonon coupling compounds due to vacancies.

We instead adopt the point of view that the metal- $d_{t_{2g}}$ -nonmetal- p interaction is crucial to the strong electron-phonon coupling in stoichiometric MoN . This feature, which is not evident in the GG expression, was first discussed in detail for NbC by Schwarz and Rösch.¹⁷ To be specific, we expect that the decrease in η will arise from contributions proportional to the t_{2g} and p DOS of the Mo and N atoms, respectively. The x dependence of η is taken in the GG-like form^{18,19}

TABLE II. Density-of-states ratios and superconducting parameters in MoN_x, based on the tight-binding CPA model. Units are as in Table I.

x	N_p^N/N	$N_{t_{2g}}^{Mo}/N$	η_N	η_{Mo}	λ_N	λ_{Mo}	λ_{tot}	ω_{log}	μ^*	T_c
1.0	0.079	0.752	5.1	13.8	0.30	1.28	1.58	275	0.139	29.4
0.9	0.067	0.733	4.3	13.4	0.23	1.03	1.26	299	0.139	24.4
0.8	0.061	0.714	3.9	13.1	0.19	0.84	1.03	326	0.139	19.7
0.7	0.053	0.691	3.4	12.7	0.15	0.70	0.85	351	0.139	14.3
0.6	0.045	0.662	2.9	12.2	0.12	0.58	0.70	374	0.139	9.0
0.5	0.036	0.629	2.3	11.5	0.09	0.47	0.56	393	0.139	4.3

$$\begin{aligned}\eta_{Mo}(x) &= N(E_F, x) \langle I_{Mo}^2(E_F, x) \rangle \\ &= N(E_F, x) \left[C_{Mo} \frac{N_t^{Mo}(E_F, x)}{N(E_F, x)} \right],\end{aligned}\quad (4)$$

$$\begin{aligned}\eta_N(x) &= N(E_F, x) \langle I_N^2(E_F, x) \rangle \\ &= N(E_F, x) \left[C_N \frac{N_p^N(E_F, x)}{N(E_F, x)} \right],\end{aligned}$$

where the constants C_i are proportional to the normalized atomic electron-ion matrix elements discussed by Pickett¹⁸ and are determined from the values of η_{Mo} and η_N at $x=1.0$. The understanding of the x dependence of η in MoN_x is simplified further by noting that the CPA calculations indicate that the total DOS $N(E_F, x)$ changes very little with x . The results of the calculation of η using Eqs. (4) are shown in Table II. We note that the value of η_N is reduced by 24% and that of η_{Mo} by 5% at $x=0.8$, and further reductions occur for smaller x 's.

Since the electron-phonon coupling constant λ is a ratio of the electronic part η and a phononic part $M\langle\omega^2\rangle$, we need to account for the variation of $M\langle\omega^2\rangle$ with x . This we include in a phenomenological model of the x dependence of the phonon spectrum.^{16,20} We assume an increase of $\langle\omega^2\rangle$ which is proportional to the vacancy concentration $1-x$. We postulate the formulas

$$\langle\omega_{Mo}^2(x)\rangle = \langle\omega_{Mo}^2(1)\rangle + (1-x)\langle\omega_{Mo}^2(1)\rangle, \quad (5)$$

$$\langle\omega_N^2(x)\rangle = \langle\omega_N^2(1)\rangle + \frac{1}{2}(1-x)\langle\omega_N^2(1)\rangle.$$

In Eqs. (5) we made a smaller change, by a factor of 2, of $\langle\omega^2\rangle$ for the optic mode. This is consistent with the analysis of experimental data in Ref. 20, and leads to an

overall 39% reduction of λ at $x=0.8$. The variation of λ with x and the resulting T_c are shown in Table II. The transition temperature $T_c \sim 29$ K that we calculated for stoichiometric MoN is drastically decreased, for the non-stoichiometric alloy MoN, down to 4.3 K at $x=0.5$.

V. CONCLUSIONS

Three types of calculations have been applied to help understand the effects of alloying and disorder in MoN. Although a general broadening of the DOS strongly decreases T_c , it will not account alone for the low measured T_c in films. Taking into account vacancies on the nitrogen sublattice leads to a consistent semiquantitative picture of the experimental data. As an example our calculations indicate that 30% vacancies on the nitrogen sublattice could decrease T_c by about a factor of 2 from our prediction for the fully ordered stoichiometric MoN. This is still a sufficiently high transition temperature to justify further experimental studies of this prototype of a material with very strong electron-phonon coupling. We wish to emphasize that in our calculations we have *not included any disorder on the Mo sublattice*. We believe that vacancies on the Mo sublattice or substitutions of Mo by N will further reduce T_c . We speculate that degradation of the Mo sublattice may contribute to the low T_c observed in recent experiments.^{4,5}

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