

Superconductivity

Nitride offers 30K transition?

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MATERIALS capable of making a transition to the superconducting state at a temperature significantly greater than the liquification temperature of hydrogen would have important applications in technology, for which reason it is disappointing that there has been no increase of the largest-known transition temperature, T_c , in the past ten years. Suggestions, on theoretical grounds, that mechanisms of superconductivity other than the interaction between phonons (lattice vibrations) and electrons could yield higher values of T_c have not so far materialized. In what follows, we argue that the B1 crystal structure of molybdenum nitride, MoN, is a prime candidate for a 'high-temperature' superconductor and that it should have a transition temperature in the region of 30K.

The quality of the numerical results of theoretical studies of the electron-phonon interaction and T_c in the past decade largely parallels the accuracy of energy-band calculations for metals and metal compounds (for reviews, see refs 1,2). The experience of our group and others suggests that the B1-structure carbides and nitrides are good candidates for materials with high T_c , and for two reasons. First, in these materials, the density of electronic states at the Fermi level, $N(E_F)$, is relatively high. Second, the electron-phonon matrix elements are large, a reflection of the strength of metal-carbon and metal-nitrogen bonds. Both these attributes favour high T_c but they also lead to structural instabilities which make it difficult to stabilize the stoichiometric structures, or magnetic instabilities which quench superconductivity.

In the past few years, we have nevertheless calculated the band structure and the superconducting properties of a number of transition-metal carbides and nitrides with NaCl structure¹⁻⁵. Since these calculations are in good agreement with experiment, we are confident of our predictions by similar calculations for other materials in the same class which have not so far been produced in the laboratory. Recently we proposed⁶ that MoN in the B1 (NaCl) structure should be a superconductor with $T_c \sim 30K$.

The equilibrium MoN phase diagram⁷ reveals a hexagonal compound, δ -MoN, at a strict one-to-one atomic ratio which is stable below 800°C, but with available methods of preparation (sputtering, electron beam evaporation, shock compression vapour deposition and ion implantation) it is not unusual to form metastable phases such as B1-structure MoN. Given the predicted high value of T_c for this material, we believe that a concerted effort to induce its formation should be undertaken.

We have calculated by the same method⁸ the electronic structure and the superconducting properties of VN, CrN, TaN and WN as well as NbN and MoN (Fig. 1a). In going from the group V to the group VI compounds, $N(E_F)$ increases substantially, which is a signal for superconductivity or, possibly, for magnetism. Note that MoN has a value of $N(E_F)$ more than twice that of NbN, which is itself a high- T_c material.

To quantify the tendency towards magnetism, we have plotted in Fig. 1b the quantity NI_{sp} , the product of $N(E_F)$ and the generalized exchange matrix element

calculated by the Stoner theory^{9,10}. CrN, with a very large $N(E_F)$, is clearly predicted to be magnetic in the B1 structure, in agreement with experiment. VN and MoN have large values of $N(E_F)$, but nevertheless MoN does not come near the Stoner criterion ($NI_{sp} > 1$) for magnetism. It has been suggested¹¹ that in VN, spin fluctuations suppress T_c , but in spite of the large value of $N(E_F)$, MoN has a much lower value of NI_{sp} , not unusual for good superconductors. We conclude that the role of spin fluctuations in MoN is not dominant and therefore leaves it as a prime candidate for high T_c .

The strength of the electron-phonon interactions assessed by $\eta = N(E_F) I_{ep}^2$ (where I_{ep}^2 is the electron-phonon scattering matrix element), reveals that both the metal and the nitrogen contributions show a very distinct maximum at MoN (Fig. 2a). It is interesting that the quantity η , unlike Stoner's $N(E_F)I_{sp}$ which scales as $N(E_F)$, does not follow $N(E_F)$. Thus CrN, despite a very large $N(E_F)$, has η smaller than that of MoN. We have also used neutron-scattering data¹² and Debye temperature results¹³ for the $Nb_{1-x}N_x$ system to estimate the force constants $M\langle\omega^2\rangle$ and hence to obtain the coupling constant λ , which reaches a pronounced maximum for MoN (Fig. 2b).

Application of the Allen-Dynes¹⁴ form of the McMillan equation gives the superconducting temperatures shown in the table. It will be seen that T_c for VN is overestimated by about a factor of two, which

Comparison of calculated and measured values of the superconducting transition temperature

	T_c^{cal}	T_c^{exp}
VN	19.7	8.6
NbN	17.1	16.0
TaN	14.6	8.2
CrN	12.4	-
MoN	29.4	-
WN	15.8	-

can be accounted for by the argument that spin fluctuations, not included in our theory, would reduce the theoretical value. The discrepancy for CrN, which is magnetic, is also explicable. Our calculation for NbN is in very good agreement with experiment¹⁵, while MoN stands out with a predicted $T_c \sim 30K$. The calculated value of T_c for TaN, approximately 15K, differs from the measured value¹⁶ of about 8K, but we believe that much of this discrepancy arises because we have estimated the phonon moments by scaling from measurements of the $Nb_{1-x}N_x$ system¹³.

Transition-metal carbonitrides often

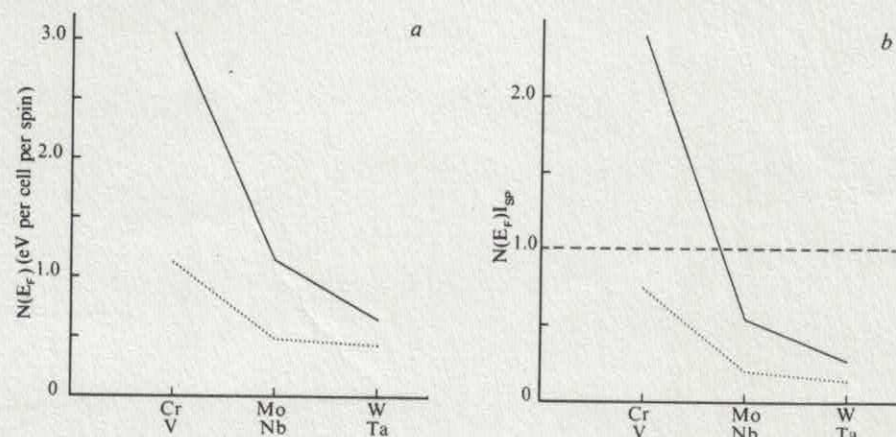


Fig. 1 a, Densities of electronic states at the Fermi level, $N(E_F)$, versus metal atom in the B1-structure nitrides. b, Stoner parameter, $N(E_F)I_{sp}$, versus metal atom in the B1-structure nitrides. $N(E_F)I_{sp} > 1$ indicates a magnetic instability. The solid (dashed) curves connect points for the Cr(V) columns in the Periodic Table.

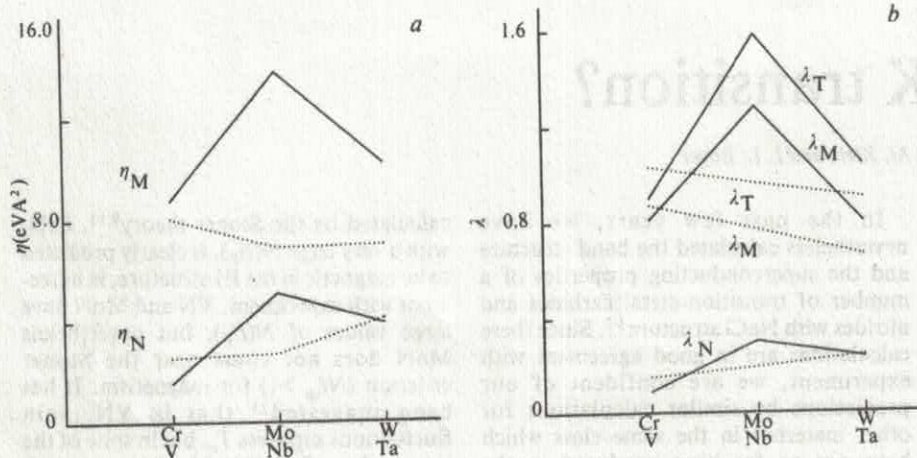


Fig. 2 *a*, Electron-phonon interaction parameters, η , for the nitrogen and metal sites in the B1-structure nitrides. *b*, Electron-phonon mass enhancement factor λ , for the B1-structure nitrides. $\lambda_{TOT} = \lambda_{MET} + \lambda_N$. The solid (dashed) curves connect points for the Cr(V) columns in the Periodic Table.

form with vacancies on the non-metal sublattice, and we have estimated the effect of nitrogen vacancies on our prediction by coherent potential approximation (CPA) calculations for MoN_x . Our model, previously applied to NbC_x and TaC_x (ref. 4), assumes that the metal sublattice remains unchanged while the nitrogen sublattice contains vacancies at random. We have used the tight-binding form of the CPA, which involves a tight-binding fit to the MoN energy bands and a subsequent determination of self-energies Σ_s and Σ_p corresponding to the s and p nitrogen orbitals. Our results for $x = 0.99, 0.98, 0.95$ show that $N(E_F)$ remains within 1 per cent of the stoichiometric value. Although E_F lies at a peak in $N(E)$, it is not a narrow peak (contrary to the case in some high- T_c compounds) and so is not sensitive to disorder. So even with a modest proportion of N vacancies, MoN should have a high T_c in the B1-lattice form.

The only experimental report of B1 MoN is that of Saur and collaborators¹⁷, who identified it as a second phase in a sample that was primarily hexagonal ('WC type'). Their value of the cubic lattice constant, $a = 4.16 \text{ \AA}$, is 2 per cent smaller than our estimated value of 4.25 \AA derived from measured lattice constants in the MoC_x and $NbC_{1-x}N_x$ systems. If 4.25 \AA is the correct value, using the lattice constant behaviour in MoC_x as a guide indicates that a sample with $a = 4.16 \text{ \AA}$ contains 30–40 per cent N vacancies. It would be very useful to have the work of Saur *et al.* verified independently. Recent experiments by Fuller *et al.*¹⁸ using radio-frequency reactive sputtering led to the discovery of a new metastable phase of hexagonal Mo_2N , but the B1 structure was not realized.

We wish, finally, to emphasize that the compounds which are known to form in both the B1 and hexagonal (WC) phases have the highest T_c in the B1 phase. For

example, WC-structure MoC has $T_c = 9K$ compared with $14K$ in the B1 structure. Considering that WC-structure MoN has been reported to have T_c of $15K$ (ref. 19), it may be anticipated that B1-structure MoN would have considerably higher T_c . These arguments, as well as the empirical rules for the carbides and nitrides²⁰, support the idea of high T_c in B1-structure MoN . □

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