Phonon and elastic instabilities in MoC and MoN

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We present several results related to the instability of MoC and MoN in the B1 (sodium chloride) structure. These compounds were proposed as potential superconductors with moderately high transition temperatures. We show that the elastic instability in B1-structure MoN, demonstrated several years ago, persists at elevated pressures, thus offering little hope of stabilizing this material without chemical doping. For MoC, another material for which stoichiometric fabrication in the B1 structure has not proven possible, we find that all of the cubic elastic constants are positive, indicating elastic stability. Instead, we find *X*-point phonon instabilities in MoC (and in MoN as well), further illustrating the rich behavior of carbo-nitride materials.

The early transition metal carbides and nitrides represent a technologically important series of materials, often revealing an interplay between their interesting properties and the incipient instabilities that seem to drive those properties.[1] The important features of these materials include extreme hardness and high melting temperatures, as well as superconductivity in many cases. In some of these materials, the atomistic properties (e.g., bonding properties) that drive particular macroscopic behaviors can also lead to instabilities that inhibit the stoichiometric B1 (sodium chloride) structure from forming. MoC and MoN are good examples of this circumstance. In this paper, we report theoretical results related to the stability of B1 MoC and MoN. We show that the elastic instability in MoN is not mitigated, but rather *enhanced*, by the application of pressure, and that the difficulty in fabricating B1 MoC is due to a phonon instability at the *X* point in the Brillouin zone (BZ). All the calculations reported here were performed with the linear-augmented-plane-wave method.[2–4]

The B1 carbides and nitrides of Zr, Nb, and Mo have very similar density of states (DOS) profiles, the main difference being a systematic increase in the DOS at the Fermi level. The same systematic trends can be seen in the lattice constants and bulk moduli. Figure 1 shows the bulk moduli of these materials as a function of the lattice constant. There is a general trend of decreasing lattice constant as the number of valence electrons increases, with the nitrides having the smaller lattice constants in the case of the isoelectronic systems (ZrN & NbC, NbN & MoC). Despite the smaller lattice constants of the nitride systems, the corresponding increases in the bulk moduli are smaller than expected compared to the isoelectronic carbide system (compare ZrN and NbC or NbN and MoC in Fig. 1). In a strict rigid-band view, the bulk moduli would be purely a function of volume, leading to a single smooth curve in Fig. 1 rather than separate curves for the carbides and the nitrides. This circumstance demonstrates the subtle differences in the bonding characteristics between the carbide and nitride systems. In the carbide systems, the covalent bonding charge between the carbon atoms is more localized and closer to the atoms than the corresponding bonding charge in the nitrides. Thus, the more itinerant, less tightly bound charge in the nitrides is more easily deformed than the covalent bonding charge in the carbides, leading to a

smaller than expected increase in the bulk modulus of the nitrides relative to the carbides.

The above considerations illustrate that, although the major contributions to the bonding and resultant properties of the carbo-nitride systems can be accounted for by general considerations of atom size and overall valence of the formula unit, the chemical composition is also important for understanding differences in the physical properties of these materials. For example, although the B1 compounds NbN and MoC have the same number of valence electrons per formula unit and very similar DOS profiles, the former can be made close to stoichiometry while the latter cannot.

The DOS for isoelectronic pairs of these compounds are qualitatively very similar, the quantitative difference being the total DOS at the Fermi level. (A representative DOS plot is shown in Fig. 2.) By definition, in a purely rigid-band picture, the isoelectronic pairs (ZrN & NbC, NbN & MoC) would be identical. While the DOS profiles look very similar and the Fermi level occurs at similar places on the DOS profile, the DOS at the Fermi level is higher in the nitride systems compared to the isoelectronic carbide systems. The DOS at the Fermi level increases systematically with the number of valence electrons (ZrC, which has only 8 valence electrons per unit cell, has the lowest DOS at the Fermi level and the highest is for MoN which has 11 valence electrons per unit cell.)

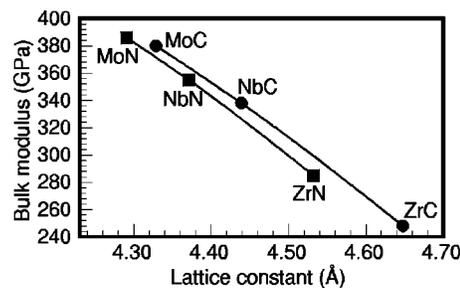The increase in the DOS at the Fermi level $[N(E_F)]$ as

FIG. 1. Lattice constants and bulk moduli of several carbo-nitrides, as calculated by the authors. The lattice constant decreases with increasing number of valence electrons per unit cell. For the isoelectronic systems (ZrN & NbC, NbN & MoC), the nitrides have the smaller lattice constant.
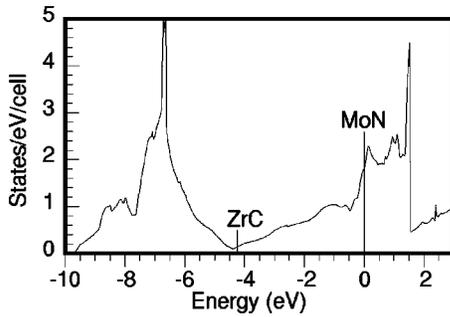
FIG. 2. Representative DOS profile for the systems considered in this paper. The DOS looks similar for all six of the systems considered here, the main differences being the position of the Fermi level and value of the total DOS at the Fermi level.
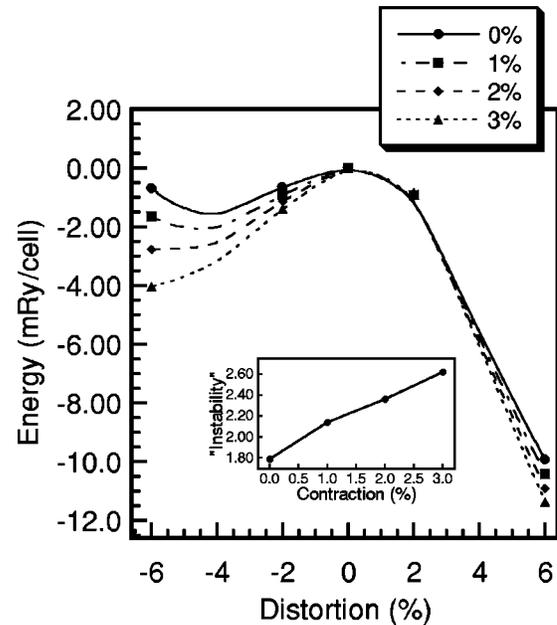

FIG. 3. Pressure dependence of the elastic instability of B1-MoN. To simulate the high-pressure behavior, the lattice constant was contracted. As pressure increases, the increasing negative curvature of the energy indicates that the instability is *enhanced* by pressure. The second-order term of a polynomial fit to each case is taken as a measure of instability and shown in the inset as a function of contraction (pressure).

the valence is increased is a rigid-band-like effect resulting from the positive slope of the DOS as a function of energy in this energy range, while the increase between isoelectronic pairs is a chemical effect due to the bonding differences between a nitride and its isoelectronic carbide. This increase in $N(E_F)$ is reflected in the superconducting transition temperatures in the series up to NbN. (NbN has the highest T_c [17 K] of the B1 superconductors.) Using simple BCS arguments, it is expected that T_c will increase with electron count due to the larger values of $N(E_F)$, resulting in T_c being higher for the nitrides. However, in B1-MoC and B1-MoN samples, the stoichiometry is poor and/or there are a large number of defects. Consequently, the superconducting transition temperatures in MoC and MoN are much lower than predicted from the perfect crystal DOS arguments using quantitative rigid-muffin-tin calculations.[5]

The systematic increase in the DOS at the Fermi level [$N(E_F)$ hereafter] led to the proposal of MoN and MoC as good candidates for ''high-temperature'' superconductors.[6,7] Using results from first principles electronic structure calculations, Pickett *et al.* argued that MoN in the B1 structure was a prime candidate for a ''high-temperature'' superconductor with a predicted transition temperature of approximately 30 K.[6,7] There were two aspects of the electronic structure that motivated this prediction for MoN—the high value of $N(E_F)$ and the large electron-phonon matrix elements associated with the strong bonding in this material. Both of these features are indicative of a potentially high T_c, but they are also hallmarks of either structural instabilities that can frustrate the formation of stoichiometric structures, or of magnetic instabilities that can destroy superconductivity.

Experimentally, it was found that these features lead instead to structural instabilities in B1-MoN that are manifested by the fact that only highly N deficient or vacancy/defect-rich B1 structures have been made in the laboratory.[8–18] Alternatively, the more thermodynamically stable hexagonal phase of MoN is often formed close to stoichiometry. Similar systems, such as NbC and NbN, which exhibit superconductivity are also prone to poor stoichiometry and must be prepared carefully to obtain a ratio of Nb to carbon or nitrogen that is close to one-to-one.[19] Some workers tried to improve the crystals by applying pressure in an attempt to drive nitrogen defects from interstitial sites into the nitrogen sites of the ideal crystal. Unfortunately, this re-

sults in a hexagonal structure less favorable for high T_c.[9,12,13,20]

In an effort to explain the experimental ''instability'' of B1-MoN, Chen *et al.* performed theoretical studies of the cubic elastic constants for MoN.[21] They found that the cubic elastic constant C_{44} for MoN was negative, indicating an instability. It is perhaps not unreasonable that a metastable state might exist, however, given the successes in forming metastable phases of other carbo-nitride compounds,[19] and others have suggested that the C_{44} instability may be mitigated in MoN by applying high pressures. To test this, we calculated the change in energy as a function of a monoclinic strain at various pressures. The results are shown in Fig. 3. As is evident from the figure, the instability persists and even *increases* at pressures high enough (above 400 GPa) to contract the lattice constant by 3%. This indicates that any attempts at fabricating a metastable phase, even at the highest available laboratory pressures, will be unsuccessful.

Because the stability of MoC samples is not much better than that of MoN, and the predicted superconductivity transition temperature is smaller than expected,[22] it is natural to suspect that C_{44} for MoC also reveals the same instability observed in MoN. However, our calculations show that for MoC the C_{44} elastic constant is large and positive. The other two elastic constants, C_{11} and C_{12}, are also relatively large and positive, indicating an elastically stable structure.

Given that the elastic constants show MoC to be stable, the question arises: why can stoichiometric B1-structure MoC not be made? In particular, is B1-MoC a possible metastable phase, or is it intrinsically unstable for some reason other than elastic behavior? Because two related systems
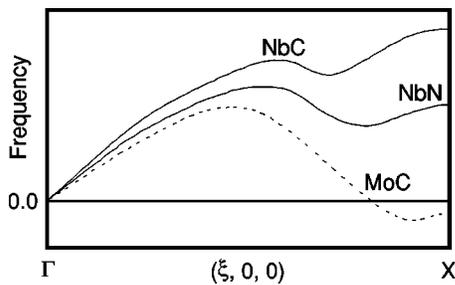
FIG. 4. Schematic diagram of the increasing instability of longitudinal-acoustic phonons in NbC, NbN, and MoC. The small anomaly in NbC at approximately $k = 0.7(2\pi/a)$ along ΓX becomes quite pronounced in NbN and shifts towards the X point. Presumably, the softening becomes so pronounced in MoC (indicated by the dotted line) as to render the structure unstable, explaining the experimental difficulty in forming MoC stoichiometrically in the B1 structure.

(NbC and TaC) exhibit phonon anomalies (dips in the phonon dispersion curves), as a first step toward answering this question, we examined the phonon frequencies of MoC at selected points in the Brillouin zone. Using the frozen phonon approach, we first determined the phonon frequencies of MoC and MoN at the Γ point, and NbC at the X point to compare with experiment[23] and previous calculations[24,25] as a check on our method. Our results are within a few percent of the experimental results as well as Savrasov's calculations for NbC.[24] The frequency of the calculated zone center optical phonon in MoC shows no indication of a phonon anomaly and is very close to that of NbC (as one might expect). On the other hand, the frequency of the calculated zone-center optical phonon in MoN is less than half that of MoC and NbC. (Of course, zone-center *acoustic* modes in MoN are unstable as shown by the C_{44} calculation.)

Even when a high $N(E_F)$ does not indicate a structural or magnetic instability, it may indicate anomalous phonons. Though NbC is quite stable and samples can be fabricated with good stoichiometry, the phonon spectrum contains a very distinct anomalous region near $k = 0.7$ $(2\pi/a)$ along ΓX that is related to Fermi surface nesting as shown by Gupta and Freeman[26] and Klein *et al.*[27] In the rigid band picture, NbN is similar to NbC but with an extra valence electron per unit cell. Adding an extra electron to the system (NbC$\rightarrow$NbN) causes more hybridized Nb D/nonmetal p states to be occupied which leads to an increase in $N(E_F)$. The anomalous region in the phonon spectrum becomes more pronounced and shifts toward the X point (schematically indicated in Fig. 4). If the phonon spectra of these carbo-nitride systems also follow systematic trends as for the lattice constants, bulk moduli, and $N(E_F)$, then it is reasonable to expect that the anomalous region of the phonon spectrum may become even more pronounced in MoC—perhaps even to the point that some phonon modes become unstable

causing the crystal to spontaneously distort at finite temperatures. This is schematically indicated in Fig. 4. Given these ideas, a good candidate BZ region for phonon instabilities in MoC would be that near the X point.[28]

To test this hypothesis, we calculated the frequencies of the optical and acoustic longitudinal phonons at the X point for MoC. Our calculations show a frequency for optical longitudinal phonons that is nearly half that of NbC, and the calculated frequency for acoustic longitudinal phonons is imaginary (367 cm^{-1}) indicating that these latter phonons are unstable at the X point. It can be reasonably surmised, then, that there exists a finite region of the spectrum near the X point for which the *acoustic* phonons are unstable. This is consistent with the experimental instability that exists despite the local-density approximation-fact that based calculations of the elastic constants indicate that B1-MoC is elastically very stable. While the Fermi surfaces of MoC and MoN which we calculated (not shown here) show indications of nesting effects with a wave vector at or near the X point, the nesting features are not as pronounced as those found in NbC and TaC.[26,27] The phonon anomalies cannot be explained as simple nesting effects; they are a complicated combination of nesting (phase-space considerations) and bonding (the strength of the electron-phonon matrix elements).

In summary, we discussed systematic trends in some of the physical properties in the series of compounds TC and TN, $T = Zr$, Nb, Mo. Lattice constants, bulk moduli, DOS at the Fermi level, etc., change systematically through the series. Corresponding to these systematic changes, the superconducting transition temperatures of the materials increase with increasing numbers of electrons per unit cell, but the compounds become increasingly unstable through the series.

While Chen *et al.* showed that perfectly stoichiometric B1-MoN was unstable, we have also shown that, contrary to conjectures in the literature, these instabilities are not mitigated by increased pressure—that is, the C_{44} instability actually is enhanced by the application of hydrostatic pressure.

Unlike MoN, there is no indication of a similar elastic instability in B1-structure MoC despite the fact that fabrication of high quality MoC crystals has been unsuccessful. We have shown that this experimental instability is related to an extreme phonon softening near the X point. Consequently, as with MoN, a stable state of B1-MoC cannot be expected.

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[1] L. E. Toth, *Transition Metal Carbides and Nitrides* (Academic Press, New York, 1971).

[2] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[3] David J. Singh, in *Planewaves, Pseudopotentials, and the LAPW Method* (Kluwer Academic Publishers, Boston, 1994).

[4] P. Blaha, K. Schwarz and J. Luitz, WIEN97, Vienna University of Technology, Vienna 1997; updated version of P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).

[5] See, e.g., B. M. Klein and W. E. Pickett, in *Superconductivity in d- and f-band Metals 1982*, Proceedings of the IV Conference, edited by W. Buckel and W. Weber (Kernforschungszentrum Karlsruhe GmbH, Karlsruhe, 1982), and references therein.

[6] W. E. Pickett, B. M. Klein, and D. A. Papaconstantopoulos, Physica B & C **108**, 667 (1981); D. A. Papaconstantopoulos, W. E. Pickett, B. M. Klein, and L. L. Boyer, Nature (London) **308**, 494 (1984).

[7] Y. Zhoa and S. He, Solid State Commun. **45**, 281 (1983).

[8] E. J. Saur, H. D. Schechinger, and L. Rinderer, IEEE Trans. Magn. **MAG-17**, 1029 (1981).

[9] H. Ihara *et al.*, Phys. Rev. B **32**, 1816 (1985); **31**, 3177 (1985); IEEE Trans. Magn. **MAG-23**, 1101 (1986).

[10] N. Savvides, J. Appl. Phys. **62**, 600 (1987).

[11] G. Linker, H. Schmidt, C. Politis, R. Smithey *et al.*, J. Phys. F **16**, 2167 (1986); G. Linker, R. Smithey, and O. Meyer, *ibid.* **14**, L115 (1984).

[12] A. Bezinge, K. Yvon, J. Muller, W. Lengaurer, P. Ettmayer, Solid State Commun. **63**, 141 (1987).

[13] B. Cendlewska, A. Morawski, and A. Misiuk, J. Phys. F **17**, L71 (1987).

[14] S. Ohshima, R. Satoh, and T. Wakiyama, Jpn. J. Appl. Phys., Suppl. **26**, 957 (1987).

[15] J. Jung, A. Morawski, and J. Karpinski, Physica B & C **139**, 639 (1986).

[16] A. Morawski, B. Cendlewska, and B. Gren, Physica B & C **139**, 645 (1985).

[17] L. L. Boyer, H. Krakauer, B. M. Klein, W. E. Pickett, and C. S. Wang, Physica B & C **135**, 252 (1985).

[18] M. Kagawa, T. Ono, K. Fukuoka, Y. Syono, M. Ikebe, and Y. Muto, Jpn. J. Appl. Phys., Part 2 **24**, L747 (1985).

[19] There have been reports that the stable phase of stoichiometric NbN (and TaN) is also hexagonal. This explains the experimental difficulty of fabricating NbN crystals in the cubic phase— stoichiometric B1-NbN is only metastable and must be made using ''nonequilibrium'' techniques. References related to the hexagonal phases of NbC and TaC include G. V. Samsonov and I. M. Vinitskii, *Handbook of Refractory Compounds* (Plenum, New York, 1980); N. Schönberg, Acta Chem. Scand. **8**, 199 (1954).

[20] D. A. Papaconstantopoulos, W. E. Pickett, B. M. Klein, and L. L. Boyer, Phys. Rev. B **31**, 752 (1985).

[21] Jing Chen, L. L. Boyer, H. Krakauer, and M. J. Mehl, Phys. Rev. B **37**, 3295 (1988).

[22] Typical values are approximately 12–14 K, whereas predictions for T_c are 20 K or higher. For example, see Ref. 2. Experimental results can be found in E. L. Haase, J. Low Temp. Phys. **69**, 245 (1987), and many others.

[23] H. G. Smith and W. Gläser, in *Phonons*, Proceedings of the International Conference in Rennes, edited by M. A. Nusimovici (Flammarion, Paris, 1971).

[24] S. Y. Savrasov, Phys. Rev. B **54**, 16 470 (1996).

[25] W. Weber, in *Superconductivity in d- and f-band Metals*, Proceedings of the Conference on Superconductivity at UC San Diego, edited by H. Suhl and M. B. Maple (Academic Press, New York, 1980).

[26] A. J. Freeman and M. Gupta, Phys. Rev. Lett. **37**, 364 (1976).

[27] B. M. Klein, L. L. Boyer, and D. A. Papaconstantopoulos, Solid State Commun. **20**, 937 (1976).

[28] Another reason for starting with the X point was that our calculations of the generalized susceptibility for MoN revealed a strong peak around the X point indicating to us that the X point was a likely location in the spectrum for an instability to occur in MoC as well.

[29] H. T. Stokes and D. M. Hatch, For more information, visit http://www.physics.byu.edu/~stokesh/isotropy.html