High-pressure synthesis and study of low-compressibility molybdenum nitride (MoN and MoN$_{1-x}$) phases

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We report the compressibility of the stoichiometric hexagonal δ phase of MoN that is a well-known hard material that becomes superconducting below $T_c = 12$ K. The measured bulk modulus is $K_0 = 345(9)$ GPa and $K_0' = 3.5(3)$. We also report the compressibility of the non-stoichiometric cubic $B1$ structured γ-Mo$_2$N phase, that has a lower bulk modulus [$K_0 = 301(7)$ GPa, assuming $K_0' = 4$]. The difference in bulk modulus is due to the difference in structure and the cohesive energy between the two phases.

INTRODUCTION

Transition metal carbides and nitrides form refractory high-strength high-hardness materials, with large values of the cohesive energy (E_c). These materials are expected to be highly incompressible (Fig. 1), consistent with the empirical relationship that relates the cohesive energy, the molar volume (V_m), and the zero-pressure bulk modulus (K_0):

$$K_0 = c \frac{E_c}{V_m}. \tag{1}$$

In this expression, c is a constant with a value between 2–4.[1] Transition metal nitrides and carbides have structures that are based upon a hexagonal or cubic sublattice formed by the metal atoms, with interstitial sites that are fully or partially occupied by N or C atoms. In the case of molybdenum nitrides, the γ-Mo$_2$N phase contains Mo atoms arranged in an fcc lattice, and up to 50% of the octahedral interstices are filled with N atoms. The stoichiometric δ-MoN phase contains Mo atoms arranged in a simple hexagonal (sh) pattern. This polymorph contains N atoms occupying trigonal prismatic sites between the Mo metallic planes. Preparation via solid state methods under normal laboratory conditions first results in a disordered material belonging to the $P\bar{6}m2$ space group which has the WC structure. Annealing under high P_{N2} conditions, or following synthesis at high pressures, yields an ordered compound δ-MoN with space group $P6_3mc$. The unit cell a and c parameters are doubled compared with those of the WC structured MoN, due to the ordering pattern of N atoms in the trigonal prismatic sites and the slight distortion in the Mo atom positions. The assignment of the structure is somewhat controversial: we have recently confirmed the original assignment of the space group and atomic position parameters by a combination of *ab initio* theoretical calculations and combined x-ray and neutron structure refinement.[2]

Surprisingly, very few studies of the compressibility of such high-hardness materials have been carried out to date,

although other bulk mechanical properties have been determined.[3,4] Here we report measurement of the bulk modulus for the ordered hexagonal phase of stoichiometric molybdenum nitride (δ-MoN).

EXPERIMENTAL

The compressibility of δ-MoN was studied using angle-dispersive x-ray diffraction in a diamond anvil cell (DAC). The starting material consisted of the stoichiometric disordered phase of δ-MoN (i.e., with a random arrangement of the N atoms in the structure, and a low degree of crystallinity) prepared by solid state synthesis (ammonolysis of MoCl$_5$ at high temperature[5]) as the starting material, that was laser heated at 5.6 GPa and 2500 °C in order to transform it into the ordered δ-MoN phase (ordering the nitrogen atoms induces a doubling of the a and c axes, and results in a sample with excellent crystallinity).[6–8] The diamond culet faces were 200 μm in diameter, and the sample was contained
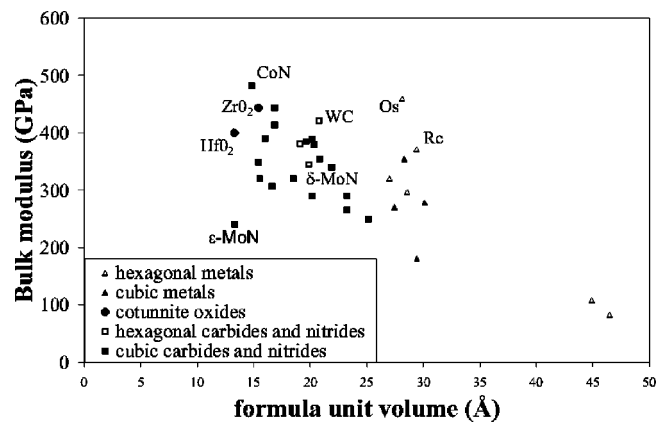

FIG. 1. Plot of the bulk modulus of several metals and binary transition metal nitrides and carbides as well as high-hardness dense oxides as a function of the unit cell volume (taken per metal atom in the formula unit) (Refs. 1, 15–19). We note that the cubic nitride CoN is predicted to have K_0 greater than that of Os.
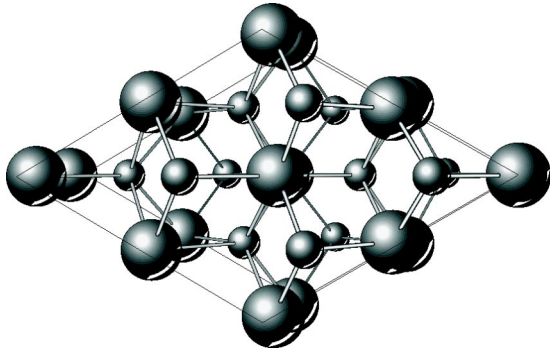
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FIG. 2. Crystal structures of hexagonal δ-MoN: the thermodynamically stable phase under ambient conditions and up to about 40 GPa. The large spheres represent the Mo atoms and the small spheres represent the N atoms. The Mo atoms form a simple hexagonal lattice with N atoms occupying half of the interstitial sites.

within a 90 μm hole drilled in a Re gasket. In a second set of experiments, a sample of γ-Mo$_2$N was synthesized from chemical precursors in a piston cylinder device (MoCl$_3$ + Zn$_3$N$_2$ at $P \sim 1$ GPa and $T = 700\,°$C),[9] and studied at high pressure in the DAC. In that set of experiments the diamonds had a 300 μm culet, and the sample was loaded in a Re gasket with a 130 μm hole. The samples were all cryogenically loaded with N$_2$ as a pressure medium along with ruby chips as the pressure sensor.[10] Fixed wavelength angular dispersive diffraction studies were performed at the APS sector 13 (GSECARS) ($\lambda = 0.04246$ nm), and also at the UK Synchrotron Radiation Source (SRS Daresbury, station 9.1, UK) ($\lambda = 0.04654$ nm). At APS, the x-ray beam was focused to ~10–20 μm using Kirkpatrick-Baez mirrors and clean-up slits. At SRS, the beam was defined using a 75 μm diameter pinhole. Two-dimensional x-ray data obtained from the angle-dispersive experiments were integrated around the diffraction rings and transformed into 1D plots using FIT2D (Ref. 11) for the data collected at APS and using EDIPUS for the data collected at the SRS.
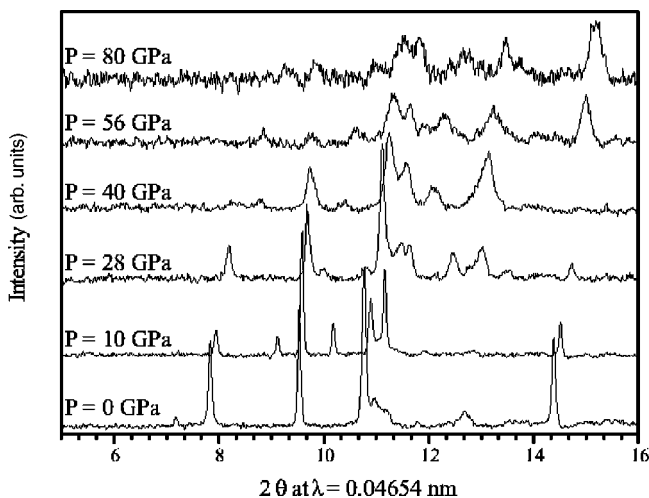

FIG. 3. X-ray diffraction patterns of δ-MoN collected at the SRS at a wavelength $\lambda = 0.04653$ nm as a function of pressure.
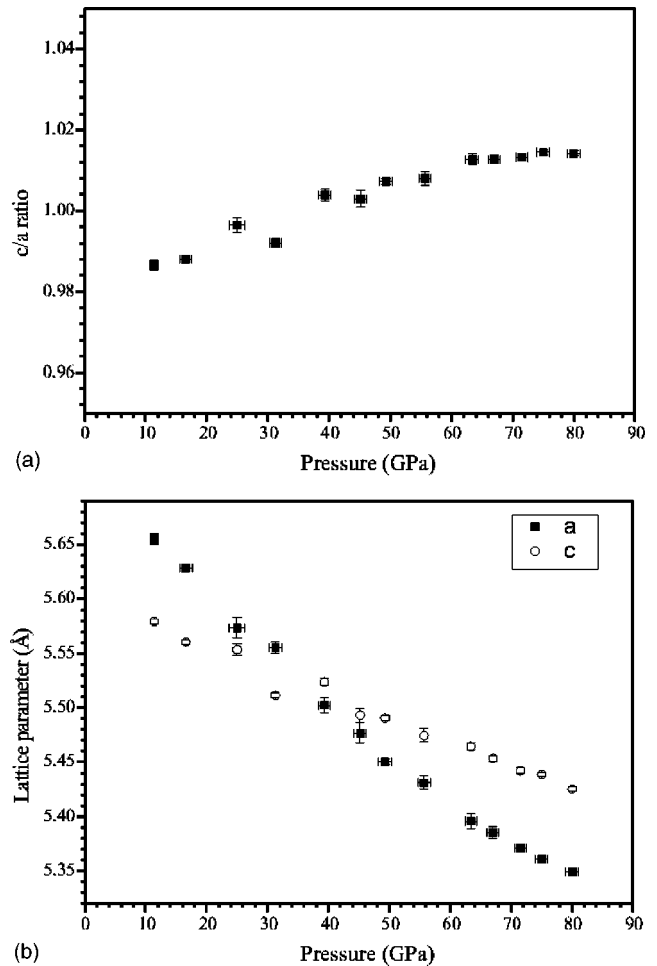

FIG. 4. (a) Plot of the experimentally measured c/a ratio for δ-MoN as a function of pressure, showing the structural stability of this phase upon compression. (b) Plot of the a and c lattice parameters as a function of pressure for δ-MoN.

RESULTS

The ordered δ-MoN phase at ambient pressure has a crystal structure [space group $P6_3mc$ (186)] that is related to that of NiAs doubled along the a axis (Fig. 2). The Mo atoms are in the $2a$ (0,0,1/4) and $6c$ (0.49,0.51,1/4) sites and the N atoms are in the $2b$ (1/3,2/3,1/2) and $6c$ (0.1667,0.8333,0) sites, as reported by Bezinge *et al.*[6] Figure 3 shows selected spectra of δ-MoN as a function of pressure. Fitting to the x-ray diffraction patterns at each pressure led to the determination of the lattice parameters and volume of δ-MoN as a function of pressure. The measured c/a ratio always remained close to unity, although it increased slightly as a function of pressure, showing that the δ-MoN is slightly more compressible along the a axis than along c [Fig. 4(a)]. Below 40 GPa, c is slightly longer than a, and above 40 GPa, c becomes the shortest axis [Fig. 4(b)].

Figure 5(a) shows V/V_0 as a function of pressure. Fitting the data to the Birch-Murnaghan equation of state gives $K_0 = 345(9)$ GPa with $K_0' = 3.5(3)$. Representing the data in terms of the Eulerian strain parameter (f) and normalized pressure (F), i.e.,
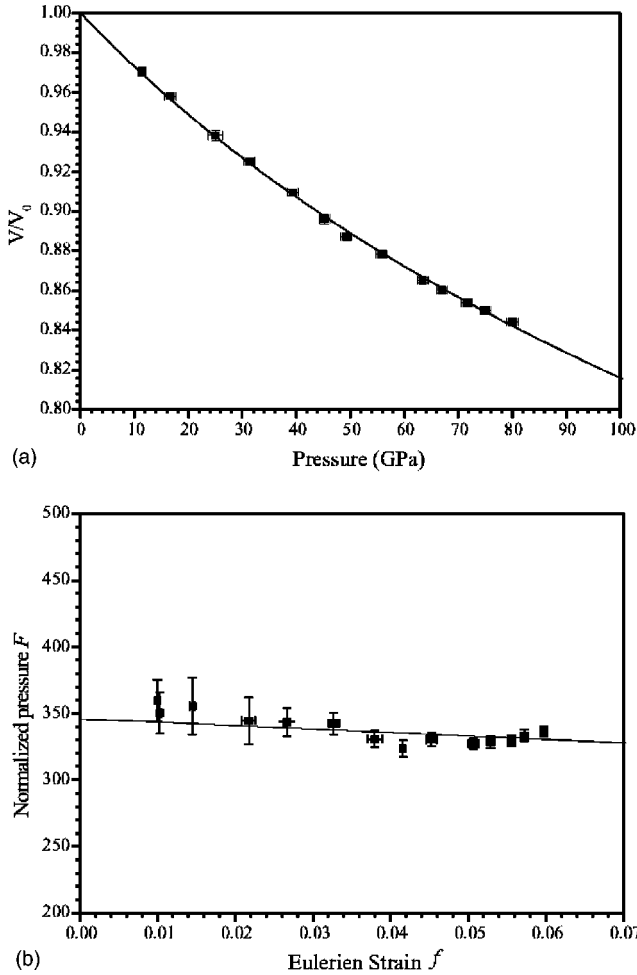
(a)

(b)

FIG. 5. (a) Plot of V/V_0 data for δ-MoN as a function of pressure with the fit of the Birch-Murnaghan equation of state for $K_0 = 345(9)$ GPa and $K_0' = 3.5(3)$. (b) Plot of the Normalized pressure (F) as a function of Eulerian strain (f) showing a slight slop of the data points consistent with the deviation of K_0' from 4 observed when fitting.

$$f = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right],$$

$$F = P[3f(1 + 2f)^{2.5}]^{-1}$$

allows us to clearly show the slight negative slope which demonstrates that $K_0' < 4.0$ [Fig. 5(b)].

In a second set of experiments we also measured the bulk modulus of γ-Mo$_2$N. The diffraction pattern of the starting material presents very broad peaks characteristic for nanocrystalline materials. Due to the broadness of the peaks, the accuracy of the lattice parameter refinements is not as good as in the previous set of experiments, and the data points on the V/V_0 plot show more scatter. The fit of the data to a second order Birch-Murnaghan equation of state yields a bulk modulus $K_0 = 301(15)$ GPa (Fig. 6).

The difference in the value of the bulk modulus between the two phases is due to both the increase of bonding elec-
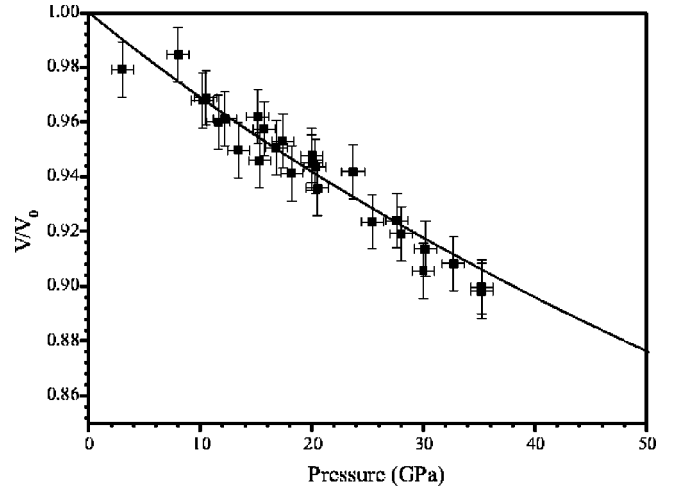

FIG. 6. Plot of V/V_0 for the γ-Mo$_2$N sample as a function of pressure with the fit of the Birch-Murnaghan equation of state for $K_0 = 301(7)$ GPa and $K_0' = 4$.

trons (linked to the increase in the N content) and also to the changes in the structure. The electronic density of states function in the two structures is very different, so that the cohesive energy and thus the bulk modulus are expected to differ substantially. As a comparison, elemental Mo has a body centred cubic structure, and has a bulk modulus of $K_0 = 267$ GPa with $K_0' = 4.5$.[12] The molybdenum nitride phases are less compressible than the pure metal, due to electron filling from the N atoms into the antibonding states above the pseudogap. Hexagonal carbides and nitrides such as WC (Ref. 13) and TaN (Ref. 14) have a bulk modulus comparable to that of δ-MoN.

In conclusion, we have measured a remarkably high value of the bulk modulus for the well-known high-hardness material δ-MoN [$K_0 = 345(9)$ GPa and $K_0' = 3.5(3)$]. We have also measured the bulk modulus for the cubic γ-Mo$_2$N phase [$K_0 = 301(7)$ GPa and $K_0' = 4$], that has a $B1$ structure with a N-deficient sublattice. Those results confirm the fact that nitrides count among the least compressible materials, consistent with their high hardness values.

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