

Compressibility of cubic vanadium mononitride

D. DZIVENKO^{1(a)}, A. ZERR², N. GUIGNOT^{3(b)}, M. MEZOUAR³ and R. RIEDEL¹

¹ *FB Material- und Geowissenschaften, Technische Universität Darmstadt - Petersenstr. 23, 64287 Darmstadt, Germany, EU*

² *LPMTM-CNRS, Institut Galilée, Université Paris Nord - 99 av. J. B. Clément, 93430 Villetaneuse, France, EU*

³ *ESRF - BP 220, 38043 Grenoble Cedex, France, EU*

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Abstract – The equation of state of vanadium mononitride with a cubic rock-salt structure, δ -VN, was measured on quasi-hydrostatic compression in a diamond anvil cell to 29 GPa. From these data the bulk modulus of δ -VN, $B_0 = 300(6)$ GPa, and its first pressure derivative, $B'_0 = 3.6(6)$, were obtained. A comparison of the available data on B_0 for δ -TiN, δ -ZrN, δ -HfN and δ -VN, extended by the present result, indicates a systematic agreement between the experimental B_0 -values from compression measurements and theoretical predictions based on the generalized gradient approximation (GGA) method. An increase of B_0 with decreasing zero-pressure specific volume, earlier suggested for the group-4 and -5 transition metal mononitrides, is not confirmed.

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Introduction. – Group-4 and -5 transition metal mononitrides with a cubic rock-salt structure (δ -MN, where M = Ti, Zr, Hf, V, Nb or Ta) possess useful mechanical, thermal, chemical, electro-magnetic and decorative properties. They find a broad industrial application as hard wear-resistant coatings of cutting tools, corrosion and abrasion protection layers on mechanical and optical components, diffusion barriers and superconductors in microelectronics [1–4]. Although many of structural and functional properties of these materials are well investigated, the information on such a fundamental property as the bulk modulus, B_0 , remains scarce and contradictory (table 1).

Theoretical calculations applying both the local density approximation (LDA) and the generalised gradient approximation (GGA) have shown that B_0 of the group-5 element mononitrides systematically exceeds that of group 4 [5–8]. Among the group-5 element mononitrides, the LDA method gives for δ -VN and δ -TaN the highest bulk moduli, up to ~ 380 GPa. This value is similar to B_0 of cubic BN (369–382 GPa) [9], the second hardest material after diamond. The existing experimental B_0 values for δ -MN obtained by acoustic measurements or

from phonon dispersion curves [8,10,11] do not show any correlation with the calculations and with each other (fig. 1, table 1). In contrast, B_0 of δ -TiN, δ -ZrN and δ -HfN derived from the experimental equations of state (EoS), *i.e.* the dependence of volume on pressure $V(P)$ [8,12], are in reasonable agreement with those calculated employing the GGA [5,6] (fig. 1, table 1). This method of the B_0 measurement is the most reliable because the unit cell volume V is measured at high pressures (HP) via X-ray diffraction (XRD) and the obtained values are not biased by sample imperfections such as pores, cracks, impurities (as could be the case in acoustic measurements) or by theoretical models (needed for treatment of the phonon dispersion data). The only earlier HP-XRD study for a group-5 mononitride, namely for δ -NbN, yielded $B_0 = 348$ GPa [8] which lies at the upper bound of the theoretical values from the LDA calculations [5,7,8]. Comparing their results for δ -NbN, δ -ZrN and δ -HfN, Chen *et al.* [8] suggested a systematic increase of B_0 with decreasing zero-pressure specific volume V_0 . Extrapolation of this near linear dependence to δ -VN (having the unit cell volume $V_0 = 70.694 \text{ \AA}^3$) would result in the bulk modulus around 450 GPa (fig. 1), similar to that of diamond (433–442 GPa) [9]. However, this consideration does not hold if results of the HP-XRD measurements for δ -TiN ($V_0 = 76.225 \text{ \AA}^3$) are included because a significantly lower value of $B_0 = 289$ GPa was

^(a)E-mail: dzivenko@materials.tu-darmstadt.de

^(b)Present address: Synchrotron SOLEIL - L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France, EU.

Table 1: Experimental and theoretical values of bulk modulus B_0 (GPa) and its first pressure derivative B'_0 (given after slash if available) for cubic rock-salt type mononitrides of group-4 and -5 transition metals.

	Experimental			Theoretical	
	HP-XRD ^a	acoustic methods	phonon dispersion ^b	GGA ^c	LDA ^d
VN	300(6)/3.6(6) ^e 296(2)/4 fixed ^e	268 ^f		333 ^g , 313 ^h	376 ^g , 383 ⁱ
NbN	348/4 fixed ^j	287 ^f , 268 ^k	292 ^j	317 ^g , 309 ^h	354 ^g , 361 ⁱ , 354 ^j
TaN				338 ^g , 329 ^h	378 ^g
TiN	289/2.5 ^l	318 ^f		286 ^g , 264 ^h	322 ^g , 331 ⁱ
ZrN	248/4 fixed ^j	217 ^k	215 ^j	264 ^g , 250 ^h	292 ^g , 290 ⁱ , 285 ^j
HfN	260/4 fixed ^j	372 ^k	306 ^j	278 ^g , 269 ^h	320 ^g , 306 ⁱ

^aCompressibility measurement by means of *in situ* high-pressure X-ray diffraction; ^belastic moduli are estimated from the initial slopes of the phonon dispersion curves obtained by inelastic neutron scattering; ^cgeneralised gradient approximation; ^dlocal density approximation; ^epresent work (numbers in parentheses represent standard error in the last digit); ^fref. [10]; ^gref. [5]; ^href. [6]; ⁱref. [7]; ^jref. [8]; ^kref. [11]; ^lref. [12].

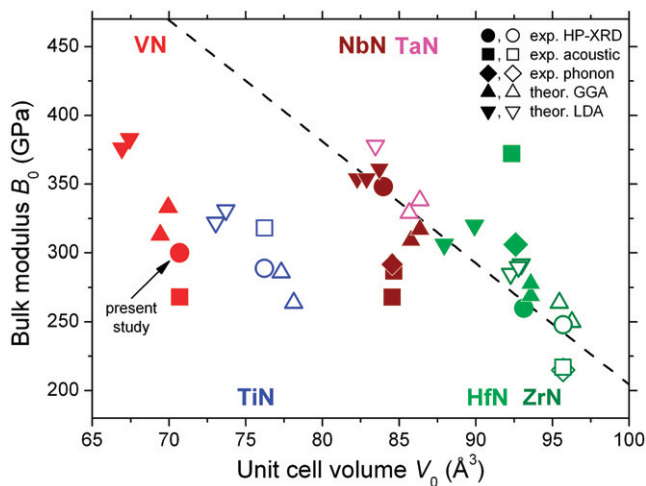


Fig. 1: (Colour on-line) Experimental and theoretical values of B_0 as a function of the zero-pressure unit cell volume V_0 for the cubic rock-salt type mononitrides of the group-4 and -5 elements (see table 1 for references). The dashed line represents a hypothetical dependence of the bulk modulus on V_0 (see text) based on the results of Chen *et al.* [8].

reported [12]. In order to clarify whether B_0 of δ -VN approaches that of diamond or is similar to 300–350 GPa, according to the GGA calculations, the room temperature EoS of δ -VN was measured in this work on compression to 29 GPa. From the experimental $V(P)$ -data the bulk modulus B_0 as well as its first pressure derivative $B'_0 = (\partial B / \partial P)_{T, P=0}$ of δ -VN were derived.

Experimental. – Powder of δ -VN (99% purity, Sigma-Aldrich) was used as a sample material in the present study. The cubic lattice parameter, $a_0 = 4.1349(9)$ Å, measured at ambient pressure indicated that our sample was stoichiometric, *i.e.* V:N = 1 [13]. The sample was compressed in a diamond anvil cell (DAC) with anvils

having culets of 350 μm in diameter. A platelet of the sample powder of about 10 μm in height (obtained by a preliminary compaction between the diamond anvils) was placed in the 120 μm hole in the preindented rhenium gasket of about 50 μm in thickness and embedded in the condensed argon, which solidifies above 1.2 GPa [14,15]. Use of argon pressure medium provided quasi-hydrostatic load conditions up to maximal pressure of 29 GPa [16,17]. It was shown in ref. [17] that in solid argon compressed up to 30 GPa the deviatoric stress does not exceed 2% of the pressure value. This estimation should be considered as the upper limit for the deviatoric stress in the present measurements since for the calculation in ref. [17] a higher value of shear modulus of solid argon from two available Brillouin measurements [18,19] was chosen. The sample pressure was determined from the earlier measured EoS of the crystalline argon [15]. The unit cell volumes of both δ -VN and crystalline argon were obtained from the angle dispersive powder XRD patterns generated using a monochromatic X-ray synchrotron beam (wavelength 0.37380(4) Å) collimated to 20 μm (beamline ID27 of the ESRF, Grenoble, France). The two-dimensional XRD patterns were collected with an image-plate detector MAR345 and converted to 1D-diffractograms (fig. 2) using the Fit2D software [20].

Results and discussion. – Typical XRD patterns measured at ambient and high pressures in a DAC are shown in fig. 2. The diffraction angles were determined by fitting the four-parameter Voigt function to each diffraction peak. By calculation of the cubic lattice parameters of δ -VN and of argon overlapping peaks were discarded from consideration. For δ -VN, the average unit cell volume and the standard error at each pressure were derived from the cubic lattice parameters calculated from each diffraction peak. Since compressed argon exhibits an elastic anisotropy [21], the maximum difference in the pressure

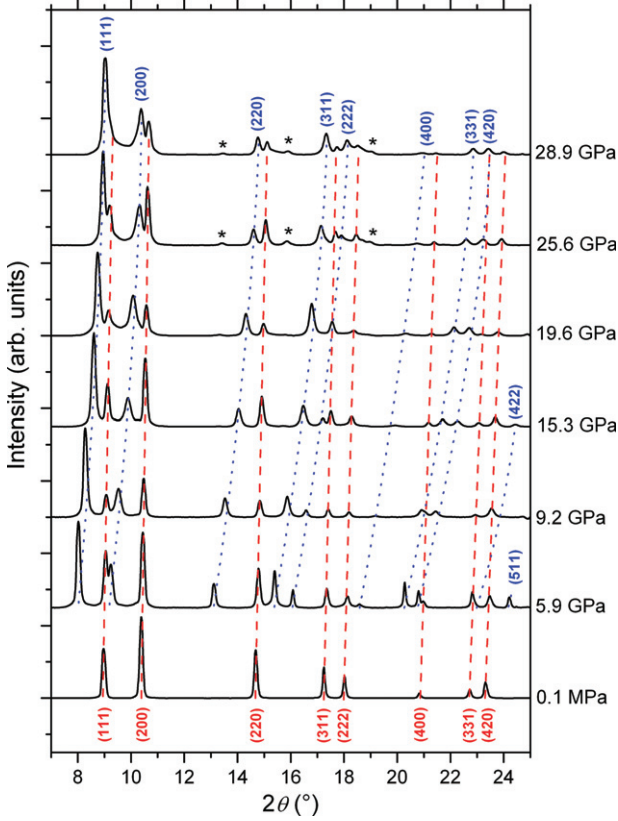


Fig. 2: (Colour on-line) Angle dispersive XRD patterns of δ -VN measured at ambient conditions and on compression in a diamond anvil cell. Evolution of the diffraction peaks of δ -VN and of crystalline argon is indicated by dashed (red) and dotted (blue) guide lines, respectively. The asterisks indicate diffraction peaks from the rhenium gasket.

values calculated for each diffraction peak of solid argon was taken as the pressure uncertainty.

For examining the measured $V(P)$ -data (fig. 3), we used the third-order Birch-Murnaghan equation of state [22],

$$P = 3B_0 f(1+2f)^{5/2} [1 + \frac{3}{2}(B'_0 - 4)f], \quad (1)$$

written in terms of the Eulerian strain $f = [(V/V_0)^{-2/3} - 1]/2$ where V_0 and V are the unit cell volumes at zero pressure and high pressure, respectively. In order to derive the bulk modulus, B_0 , and its first pressure derivative, B'_0 , the normalized pressure was written as $F = P/[3f(1+2f)^{5/2}]$. Such $F(f)$ -representation of the compression data is expected to be linear with the intercept with F -axis equal to B_0 and the slope of the line yielding B'_0 . Thus, the present $V(P)$ -data have been converted to $F(f)$ and the uncertainties in f and F have been estimated by propagation of errors [23]. The weighted linear least-squares fit [24,25] of the obtained $F(f)$ -data (fig. 3) yielded $B_0 = 300(6)$ GPa and $B'_0 = 3.6(6)$ with standard errors in the last digit given in parentheses. For the second-order Birch-Murnaghan EoS, with B'_0 fixed at 4, $B_0 = 296(2)$ GPa was obtained. In order to exclude possible influence of the chosen EoS on the derived B_0 -value, we

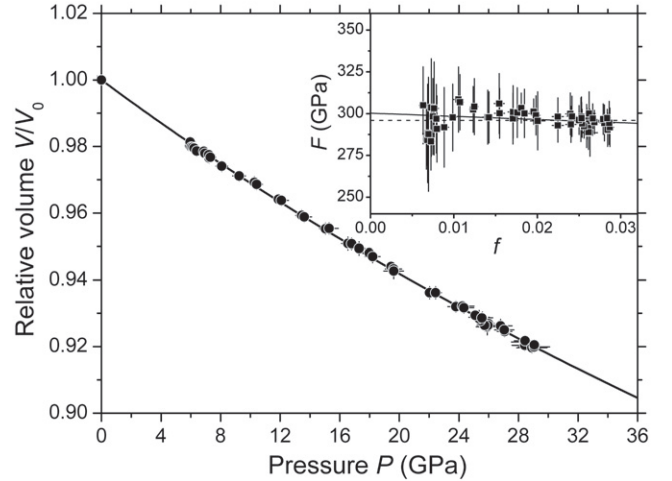


Fig. 3: Relative volume, V/V_0 , of δ -VN as a function of pressure. The experimental data are shown by solid symbols. The solid line represents the least-squares fit of the third-order Birch-Murnaghan EoS to the experimental data. Inset: compression data of δ -VN in terms of normalised pressure, F , and Eulerian strain, f (see text). The solid and dashed lines represent the least-squares fits of the third- and second-order Birch-Murnaghan EoS, respectively.

also performed the nonlinear least-squares fit of the Vinet equation [26]

$$P = 3B_0(1-x^{1/3})x^{-2/3} \exp[\frac{3}{2}(B'_0-1)(1-x^{1/3})], \quad (2)$$

with $x = V/V_0$ to our $V(P)$ -data and obtained insignificantly higher values of $B_0 = 301(3)$ GPa (with $B'_0 = 4.9(4)$) or $B_0 = 306(1)$ GPa (for B'_0 fixed at 4).

The value of $B_0 = 300$ GPa obtained for δ -VN in the present work is similar to that calculated using the GGA method. Together with the above-discussed observations for δ -TiN, δ -ZrN, and δ -HfN, our result suggests that the GGA method is the better theoretical approach for calculation of elastic moduli of transition metal nitrides than that of the LDA, at least if it also correctly predicts the equilibrium volume V_0 . Our observation does not confirm the suggestion of Chen *et al.* [8] that bulk moduli of the group-4 and -5 transition metal nitrides systematically increase with decreasing unit cell volume V_0 (fig. 1). It should be noted that not all B_0 values reported by Chen *et al.* [8] are relevant for the suggested systematics due to limitations caused by the chosen sample materials: the ambient-pressure lattice parameters reported in ref. [8] for nitrides of hafnium (4.533 Å) and niobium (4.379 Å) correspond to anion deficient nonstoichiometric compounds δ -MN $_{1-u}$ with $0.1 < u < 0.3$ [1,27,28]. Such nonstoichiometry is known to have a significant effect on elastic properties of the nitrides. In particular, recent calculations have shown that the bulk moduli of the group-4 element nitrides decrease with decreasing nitrogen content: for δ -MN $_{1-u}$ B_0 is reduced by about 8% for $u = 0.1$ and by about 16% for $u = 0.3$ with respect to that of the

stoichiometric nitride ($u=0$) [29,30]. If this also holds for the group-5 elements then the experimental B_0 of δ -HfN $_{1-u}$ and δ -NbN $_{1-u}$ reported in ref. [8] should be considered as lower limits for the stoichiometric counterparts ($u=0$). This contradicts, however, the high B_0 -value of δ -NbN $_{1-x}$ measured in ref. [8] which is closer to the theoretical values obtained using the LDA- but not the GGA-method (fig. 1, table 1). One could explain the deviation in two ways. It could be caused by experimental limitations due to the use of nonhydrostatic pressure medium (LiF) in ref. [8]: due to a low compressibility of δ -NbN, even moderate pressure gradients between the sample and the ruby chip (used in ref. [8] for the pressure determination) could significantly flatten the experimental $V(P)$ curve and thus artificially increase the B_0 -value. Alternatively, bulk moduli of the group-5 nitrides, δ -MN $_{1-u}$, could increase with u , in contrast to the group-4 nitrides. Extension of compression experiments to stoichiometric δ -TaN and δ -NbN, performed at (quasi)hydrostatic load conditions, would contribute to clarification of this controversy. The respective findings will also confirm the systematics between the theoretical B_0 -values calculated using the GGA method and the experimental counterparts, as recognised in the present study.

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