

Elastic constants of NbC and MoN: Instability of B_1 -MoN

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Total energies of MoN have been calculated for small strains from the cubic B_1 structure to orthorhombic and trigonal structures, and B_1 -MoN was found to be unstable. To check the reliability of the calculations, we have also calculated the elastic constants for B_1 -NbC and obtained good agreement with experimental results.

I. INTRODUCTION

Several recent theoretical calculations^{1,2} have indicated that molybdenum nitride (MoN) in the B_1 (rocksalt) structure would possess some extreme properties, e.g., a superconducting transition temperature (T_c) of about 29 K (which used to be considered high before the advent of the new copper-oxide ceramic superconductors). Following the initial prediction of its high T_c , several investigators³⁻⁵ have reported the synthesis of MoN in the B_1 phase; however, no high T_c has yet been found. The discrepancies between the prediction and experiments were attributed to the inevitable defects of the B_1 -MoN samples prepared with the various techniques.³⁻⁵ These defects include vacancies on the nitrogen sites, nitrogen occupation on the interstitial sites, and nitrogen incorporation on Mo sites. Some attempt was made to improve the quality of the B_1 -MoN crystals by high-pressure annealing in the hope that the nonequilibrium B_1 phase would be stabilized and that nitrogen vacancies would be filled by interstitial nitrogen atoms, because the density of the B_1 -MoN is larger than that of the equilibrium hexagonal MoN.³ However, it was found that the B_1 -phase MoN was converted mainly to the hexagonal phase under pressures as high as 6 GPa. The experiments and calculations carried out so far still appear to leave the following question open: Is the pure B_1 phase of MoN stable?

In this paper, we investigate the stability of B_1 -MoN by performing total-energy calculations for small strains of the B_1 structure. In order to estimate the reliability of the calculational results for MoN, we also calculate the total energies for B_1 -NbC versus several kinds of small strains. Analytical fittings of the total energies yield several elastic stiffness constants which are then compared with the experimental results.

II. CALCULATIONAL METHOD

The total energies are calculated within the local-density-functional approximation (LDA) using the self-consistent linearized augmented-plane-wave (LAPW) method^{6,7} with the Hedin-Lundqvist⁸ exchange-correlation potential. The calculational method employed in the program has been described in detail previously.⁷ Briefly, a LAPW basis function in the interstitial region is a plane wave which joins continuously and differentially with a scalar-relativistic solution to the spherical component of the muffin-tin potential centered on each atom. The nonspherical components of the muffin-tin potential are included in the variational determination of the eigenstates. In each iteration, we recompute the eigenstates of the core electrons which are treated fully relativistically in an atomiclike approximation. The $4p$ core states of neighboring atoms overlap slightly and about 0.3 electron per unit cell is in the interstitial region. These semicore states are treated as variational band states in a separate "energy window."

A well-converged basis set of about 200 LAPW's is used. The charge density is summed over the irreducible Brillouin zone using a set of special discrete k points: 60, 144, 204, and 288 k points for B_1 , tetragonal, trigonal, and orthorhombic structures, respectively, such that the total number of k points in the full first Brillouin zone is the same for every structure.⁹

III. RESULTS AND DISCUSSION

A. NbC

As mentioned, to check the reliability of the calculations, we calculate the elastic constants for B_1 -NbC. The results are summarized in Table I. The total energies for B_1 -NbC were first calculated as a function of the volume,

TABLE I. Elastic constants, lattice constant, and bulk modulus of B_1 -NbC.

	C_{11}	C_{12} (10^{12} dyn/cm 2)	C_{44}	a (\AA)	B (Mbar)
LAPW	6.4	1.8	1.4	4.45	3.32
Expt.	6.2	2.0	1.5	4.47	3.40

and fitted to Murnaghan's equation of state.¹⁰ The bulk modulus obtained from the fit is

$$B = \frac{1}{3}(C_{11} + 2C_{12}) = 3.32 \text{ Mbar} \quad (1)$$

and the equilibrium lattice constant is 4.45 \AA , with the rms error of the fit being about 0.03 mRy. The total energies for NbC were then calculated for small strains from the equilibrium B_1 structure to orthorhombic and tetragonal structures. A small distortion can be described by the strain tensor, $\vec{\epsilon}$, which is defined by the transformation $\mathbf{a}' = (\mathbf{I} + \vec{\epsilon})\mathbf{a}$, where \mathbf{I} is the unit matrix, \mathbf{a}' and \mathbf{a} are the new and old lattice vectors, respectively. For the orthorhombic distortion, the strain tensor is

$$\vec{\epsilon}_{\text{orth}} \approx \begin{pmatrix} 0 & \delta & 0 \\ \delta & 0 & 0 \\ 0 & 0 & \delta^2 \end{pmatrix}.$$

The change of energy density associated with the orthorhombic distortion is

$$U_{\text{orth}} = 2C_{44}\delta^2 + O(\delta^4). \quad (2)$$

For a tetragonal distortion, the strain tensor is

$$\vec{\epsilon}_{\text{tetr}} \approx \frac{1}{3} \begin{pmatrix} -\delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & 2\delta \end{pmatrix}$$

and the change of energy density is

$$U_{\text{tetr}} = \frac{1}{3}(C_{11} - C_{12})\delta^2 + O(\delta^3). \quad (3)$$

Both strain tensors keep the volumes of the distorted unit cells unchanged.

The calculated total energies for small orthorhombic distortions are shown in Fig. 1; also shown in Fig. 1 is a least-squares fit of the results to the formula (2). The fit yields the elastic stiffness constant

$$C_{44} = 1.4 \times 10^{12} \text{ dyn/cm}^2$$

with the rms error of the fit being less than 0.1 mRy.

The calculated total energies for small tetragonal distortions are shown in Fig. 2 together with their least-squares fit to the formula (3). The fit gives

$$C_{11} - C_{12} = 4.6 \times 10^{12} \text{ dyn/cm}^2$$

with the rms error of the fit being less than 0.1 mRy. Combining the above equation with (1), we have

$$C_{11} = 6.4 \times 10^{12} \text{ dyn/cm}^2,$$

$$C_{12} = 1.8 \times 10^{12} \text{ dyn/cm}^2.$$

The calculated constants for NbC are listed in Table I in comparison with the measured elastic constants¹¹ and lattice constant.¹² The excellent agreement is a confirmation of the calculational method.

B. MoN

We have calculated the total energies of MoN for small strains from the B_1 structure to orthorhombic and trigonal structures. The lattice constant used is 4.25 \AA (Ref.

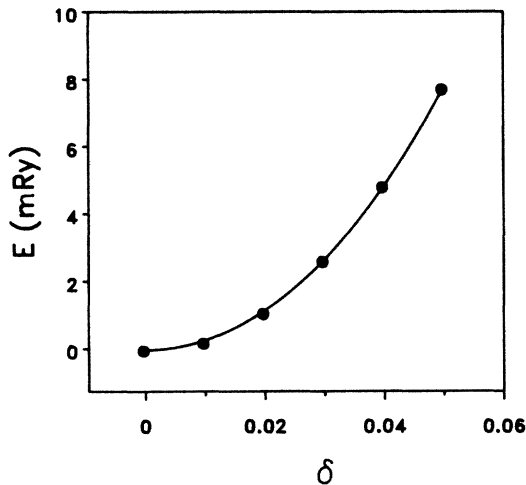


FIG. 1. The solid circles are calculated total energies for small orthorhombic distortions of B_1 -NbC (symmetric with respect to δ). The values are given relative to the energy of the B_1 structure which is -7708.40097 Ry. The line is a least-squares fit of the results.

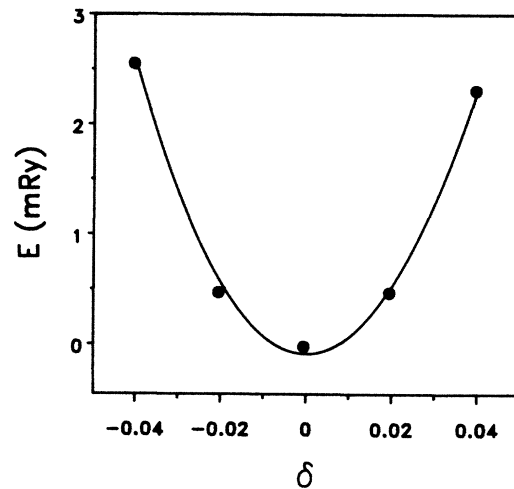


FIG. 2. The solid circles are calculated total energies for small tetragonal distortions of B_1 -NbC. The values are given relative to the energy of the B_1 structure which is -7708.40097 Ry. The line is a least-squares fit of the results.

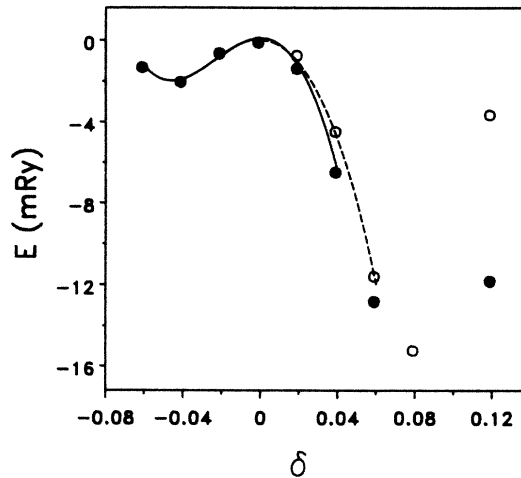


FIG. 3. The solid circles are calculated total energies for small trigonal distortions of B_1 -MoN, while the open circles are for its orthorhombic distortions. The values are given relative to the energy of the B_1 structure which is -8199.46225 Ry, and the relative energies for the orthorhombic distortions have been multiplied by 3. The lines are the least-squares fit in small regions around the B_1 structure.

1), which is within 1% of that calculated in Ref. 13. A trigonal distortion is represented by the following strain tensor:

$$\vec{\epsilon}_{\text{trig}} \approx \begin{pmatrix} \delta^2 & \delta & \delta \\ \delta & \delta^2 & \delta \\ \delta & \delta & \delta^2 \end{pmatrix}$$

and the change of energy density is

$$U_{\text{trig}} = 6C_{44}\delta^2 + O(\delta^3). \quad (4)$$

As for NbC, these strains for MoN keep the volumes of the distorted unit cells unchanged.

The total energies of MoN for small orthorhombic and trigonal distortions are shown in Fig. 3; both distortions indicate that MoN is not stable in B_1 structure and that the minimum energies are approximately at $\delta=0.08$. A least-squares fit of the total energies for the orthorhombic distortion to the formula (2) yields

$$C_{44} = -0.53 \times 10^{12} \text{ dyn/cm}^2$$

with the rms error being less than 0.1 mRy, and the corresponding fit for the trigonal distortion to (4) also yields the same value within fitting error. The elastic constant for MoN is listed in Table II together with its lattice constant and bulk modulus.¹³ The bulk modulus is positive because B_1 -MoN is stable against dilation; our primary

TABLE II. Elastic constant, lattice constant, and bulk modulus of B_1 -MoN.

	C_{44} (10^{12} dyn/cm ²)		a (Å)	B (Mbar)
LAPW	-0.53 (trig.)	-0.53 (orth.)	4.285	3.6

calculations for small tetragonal distortions also indicate that it is stable against such distortions. Thus, B_1 -MoN is at a saddle point.

The calculated elastic instability of pure B_1 -MoN is not in contradiction with the experimental synthesis of the defected B_1 -MoN crystals. Various defects such as vacancies, which have not been included in the present calculation, may stabilize the B_1 -MoN structure by increasing the total entropy and possibly lowering the total energy as in TiO and TiC (Ref. 14).

Nevertheless, the elastic instability of the B_1 phase implies that an experimental check of the initial high- T_c prediction for the B_1 -MoN could be impossible, since it appears that the B_1 -MoN crystal can only be made by tolerating certain defects which might significantly change its T_c .

IV. CONCLUSIONS

The total energies of B_1 -NbC were calculated for small strains, and the elastic constants derived from the calculated total energies for B_1 -NbC agree well with the experimental results. The same methods for B_1 -NbC are then used to calculate the total energies of MoN for small distortion from the B_1 structure to the orthorhombic and trigonal structures; the results indicate that pure B_1 -MoN is not stable. Various defects such as vacancies and disorders of the sublattices appear to play some role in leading to the stability of the reported experimental B_1 -MoN samples. It would be interesting to include certain defects in the calculation of the total energies of B_1 -MoN for small strains.

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