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NIOBIUM NITRIDE: STABILITY AND INTEGRITY OF THE "NbO PHASE"

W. E. Pickett, E. C. Ethridge and S. C. Erwin
Naval Research Laboratory, Washington DC 20375-5345, U.S.A.

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The ordered vacancy Pm3m ("NbO") structure was identified by Treece *et al.* as the phase of their pulsed laser deposited thin film samples of niobium nitride. However, the stoichiometric Pm3m phase of NbN is not easily reconciled with published local density functional results, which predict a 5% smaller lattice constant than measured and a high energy compared with the competing rocksalt phase (which is common and therefore expected to be the stable phase). Here we investigate a possible tetragonal instability of the Pm3m structure that might complicate the interpretation of xray data on the thin films. We also consider the consequences of incorporation of hydrogen into the films. Neither of these aspects is able to resolve the apparent discrepancy. Copyright ©1996 Published by Elsevier Science Ltd

1. INTRODUCTION

The fabrication and experimental study of nitrides has become an active area of research. Due to the chemical properties of nitrogen, specifically the extreme stability of the N_2 molecule in the gas phase, novel methods of sample growth are often required to produce new compounds. High pressure [1] is one method of choice, but pulsed laser deposition (PLD) offers an alternative method of incorporating N atoms within a growing solid material. The result of PLD is a film, rather thin and often not highly ordered, that may complicate the structural determination.

Treece and collaborators [2] have reported the PLD growth of NbN films. We address specifically the materials grown on MgO (100) substrates, at temperatures of 600 C in atmospheres of gaseous N_2 with 10% H_2. Such films showed superconducting transition temperatures T_c above 16 K, slightly higher than that of bulk rocksalt structure NbN_x materials ($x \approx 1$). Structural determination with xray diffraction techniques indicated a cubic cell with lattice constant of 4.44 Å, and roughly equal concentrations of Nb and N. The Pm3m structure (the stable phase of NbO) provided a reasonable interpretation of the xray intensities.

Density functional calculations within the local density approximation (LDA) are usually reliable in predicting the structural characteristics of such compounds. For example, the lattice constant of rocksalt structure NbN is predicted to within 0.3% of the experimental value. Ethridge, Erwin, and Pickett (EEP) [3] and Öğüt and Rabe [4] have presented LDA results in good mutual agreement, that predict that the lattice constant of Pm3m phase NbN should be 4.20 Å (5% smaller than the xray determination) and that the energy is 1 eV higher per NbN unit in the Pm3m phase than in the rocksalt phase. Moreover, since the lattice constant of MgO is 4.22–4.24 Å in the temperature range of the experiment, this will be maximum encouragement for epitaxial growth of Pm3m NbN at the predicted lattice constant, if indeed it can be stabilized relative to the competing rocksalt phase. These facts were used to argue [3, 4] that the films must be something more complex than Pm3m NbN. Two other crystalline forms of (nearly) stoichiometric NbN have been reported [5], the NiAs phase (P63/mmc, No. 194) and the WC phase (P6m2, No. 187). However, both of these phases are hexagonal and clearly inconsistent with the x-ray data, so other possibilities must be considered.

Here we report results of two additional studies related to possible complications that might arise: possible instability of Pm3m NbN with respect to tetragonal distortions such as might occur during epitaxial growth, and the effect of incorporation of atomic H into the NbN lattice. Neither of these possibilities resolves the outstanding questions.

2. METHOD OF CALCULATION

Local density approximation calculations with the Vosko–Wilk–Nusair [6] exchange-correlation functional were used to produce our results. We applied the full potential linearized augmented planewave method [7, 8] with sphere sizes of R_{Nb}=2.30 a.u. and R_N=1.55 a.u., with the same sphere sizes being used when the respective sites are vacant or are occupied by a H atom. The basis set cutoff was K_{max}=10 a.u.$^{-1}$, corresponding to a highly converged basis set. The Nb 3*p* semicore states were treated in the same window for maximum accuracy of the equation of state, and additional local functions were used for the Nb 3*p* and 4*d* states and for the N 2*s* states. Forty special ***k*** points were used in all calculations.

3. TREATMENT OF TETRAGONAL STRAIN

Although our calculated lattice parameter [3] of Pm3m NbN is a good lattice match with the MgO substrate (less than 1% mismatch), the earlier equation of state calculations [3, 4] with the lattice constrained to cubic form do not establish the stability of the solid against symmetry lowering strains. Earlier experience with rocksalt structure MoN [9], which turned out to be elastically unstable, indicates that transition metal nitrides especially should be checked. Whereas a much lower symmetry structure should be easy to distinguish in structural studies, a simple tetragonal strain, reconstruction, or ordered defect structure might be less obvious in Θ-2Θ scans or Φ scans.

The energy was calculated for twenty-one distinct tetragonal structures with $7.76 \leq a \leq 8.21$ a.u. ($b=a$) and $7.60 \leq c \leq 8.40$ a.u. The energies were fit to a polynomial in a and c containing all terms up through fourth order (fifteen parameters). An excellent fit was obtained, with maximum deviation of 0.28 mRy per primitive cell (the calculated energies varied by 40 mRy). The resulting energy surface is shown as a contour plot in Fig. 1. The lattice is found to respond conventionally to a uniaxial strain along the cubic axis.

The minimum occurred for a cubic structure with $a_o=c_o$=7.945 a.u.=4.203 Å, consistent with that calculated previously [3] from the cubic equation of state. The quadratic terms in the fit give the tetragonal shear modulus $C_{11}-C_{12}$=2.48 MBar and bulk modulus $B=(C_{11}+2C_{12})/3$=2.97 MBar [10].

Although the energy surface of Fig. 1 indicates stability far outside the elastic regime, we have considered the possibility of much larger strains. Our fit to the energy surface gives a Poisson's ratio P=0.32, very close to the ideal value of 1/3 for an isotropic solid. We calculated the energy at larger strains of $0.87 \leq c/c_o \leq 1.12$, with $a = b$ appropriate for volume conserving strains and for P=1/3. We find no indication of a secondary minimum in the energy surface.

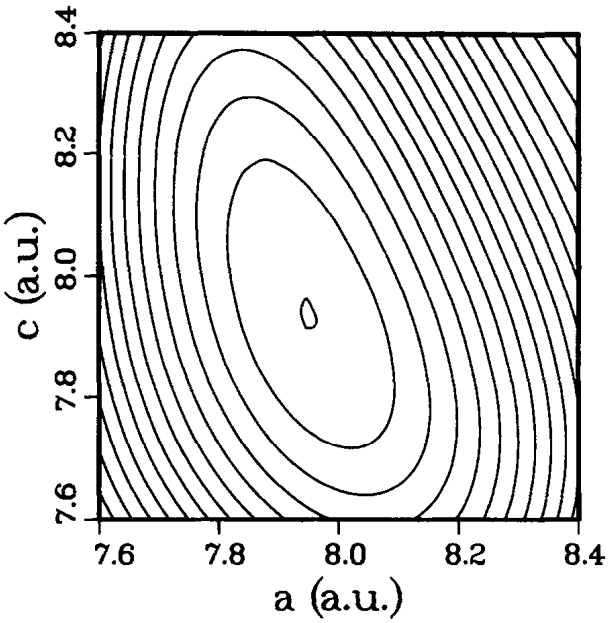

Fig. 1. A contour plot of the energy surface for tetragonal ($a = b$) strains of Pm3m NbN. The planar and axial lattice constants are denoted by a and c, respectively. The contour spacing is 5 mRy per primitive cell (three NbN units), with the minimum energy lying in the tiny contour at $a_o=c_o$=7.94 a.u.

4. STUDY OF INCORPORATED HYDROGEN

The presence of H_2 in the growth vessel suggests a mechanism that could lead to a larger lattice constant: dissociation of the H_2 molecule could be catalyzed by Nb or NbN, and atomic H incorporated in the vacant Nb and/or N sites in Pm3m NbN. The maximum increase in lattice constant should occur for maximum H incorporation, so we have looked at the case when H is placed in both vacant sites, i.e. the Pm3m compound $Nb_3N_3H_2$.

The calculations were carried out with the same parameters as described in Sec. II, and again all positional parameters are determined by the (assumed) cubic symmetry. The calculated equation of state leads to a lattice constant of 8.01 a.u.=4.24 Å, B=3.06 MBar, B′=4.55. Thus the incorporation of two H's per cell in the vacant sites leads to less than 1% increase in the lattice constant, and moderate changes in the elastic properties of Pm3m NbN, and cannot account for a phase with a 4.44 Å lattice constant.

5. SUMMARY

We have used accurate local density methods to assess if either (1) complications due to tetragonal strains, or (2) hydrogen incorporation leading to lattice expansion, can help to resolve the discrepancy between, on the one hand, the experimental assignment of a Pm3m NbN phase with a=4.44 Å, and on the other, the theoretical conclusion that this phase should have a=4.21 Å and a high enough energy relative to rocksalt NbN to make it very unlikely to occur. We find that tetragonal strains only serve to increase the energy, with no secondary minima for tetragonal strains. Incorporation of H into both the vacant sites in Pm3m NbN increases the lattice parameter by less than 1% and therefore does not help in resolving the discrepancy. We cannot rule out the possibility of the incorporation of a higher concentration of H or of incorporation of H into interstitial sites. Nb substitutionals on the N sublattice would also increase the lattice constant, but the Nb–Nb separation of 2.2 Åseems to be unreasonably short (in Nb metal the separation is 2.85 Å). None of these possibilities seems to be a likely mechanism to increase the lattice constant by 5%. Perhaps incorporation of oxygen from the substrate should also be considered.

The reliability of calculations of this type deserves comment. We use the all-electron, full potential linearized plane wave method [7, 8] which is state of the art in precision. For non-magnetic metals, semiconductors, and compounds, lattice constants are usually within 2% of the experimental value, with the calculated value nearly always being smaller than experiment. Magnetic (or nearly so) materials with open $3d$ or $4f$ shells lead to larger errors, as do alkaline and alkaline earth elemental metals. Our lattice constant [3] for rocksalt NbN, within 0.3% of the experimental value, bears out the conventional wisdom that niobium nitrides should be predicted reliably. Our recent calculations for tetragonal Nb_4N_3 [11] lead to a value of the c/a ratio comparable to the published value (within 2%). The only real conclusion is that nitrides continue to pose questions that are not easily resolved.

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