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Elastic stability and electronic structure of pyrite type PtN_2: A hard semiconductor

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Abstract

The elastic properties and electronic structure of PtN_2 with the pyrite structure (PtN_2(C2)) were studied with first-principles calculations. The crystal structure is demonstrated to be elastically stable with a lower energy than the metastable fluorite structure proposed before. The calculated shear modulus of 214 GPa suggests that PtN_2(C2) is harder than some well known hard materials such as TiN and SiC. The high elastic moduli are attributed to a stacking of corner-shared PtN_6 octahedra bonded by strong N-N covalent bonding. In contrast to the metallic fluorite-type phase, PtN_2(C2) is semiconducting in nature with an indirect band gap.

Platinum nitride is attracting increasing interest due to its fundamental and technological importance.[1-8] From the fundamental point of view, study of its structure and stability is important because the noble metals were generally thought to be impossible to form nitrides[9-10] before the synthesis of platinum nitride at high pressures and temperatures.[1] From the technological point of view, platinum nitride and other noble metal nitrides, if synthesized, may possess potentially intriguing electronic and mechanical properties. For example, platinum nitride was shown to have a bulk modulus comparable to that of cubic-BN, a known superhard material.[1]

Although successful work has been done for synthesis of platinum nitride,[1,3] the crystal structure of platinum nitride is still an open question. In the original publication for the synthesis work[1] and some following theoretical works,[4,6,8] a zinc-blende structure with a stoichiometric composition of PtN was proposed. However, more recent calculations showed that the zinc-blende PtN structure is elastically unstable.[2] A fluorite-type structure was therefore suggested with a composition of PtN_2.[2] This stoichiometry was experimentally confirmed lately.[11] In the fluorite structure (Strukturbericht symbol C1) referred to as PtN_2(C1),[12] all the N atoms occupy the tetrahedral interstitials of the Pt sublattice. The octahedral interstitials are left empty because N atoms is too small to be stabilized in the octahedral interstitials in the noble nitrides.[2] However, N atoms can indeed occupy the octahedral interstitials in the form of N_2 dimers, as in the pyrite structure (Strukturbericht symbol C2) referred to as PtN_2(C2).[12] The pyrite structure PtN_2(C2) was first suggested by Crowhurst to interpret the experimental Raman spectra.[11] In this letter, we show that PtN_2(C2) is indeed elastically stable with a lower energy than PtN_2(C1), and the calculation results match the experimental data very well. The electronic structure calculations reveal that PtN_2(C2) is a semiconductor with an indirect band gap.

The full-potential linearized augmented plane waves (LAPW) method[13] was employed in this study. This method is one of the most accurate schemes in solving the Kohn-Sham equations in density-functional theory.[14] Augmented plane waves plus local orbitals (APW+lo)[15] were used for calculating valence states, and LAPW for other states. The Brillouin zone was sampled using a modified tetrahedron method of Blöchl *et al.*[16] For accurate total energies, we used a basis size of about 150/atom and a Brillouin zone sampling of 1000 k points. A fully relativistic calculation was performed for core states, whereas the valence states were treated in a scalar relativistic scheme. Both the local density approximation (LDA)[17] and the generalized gradient approximation (GGA)[18] exchange correlation functional were employed in the present calculations.

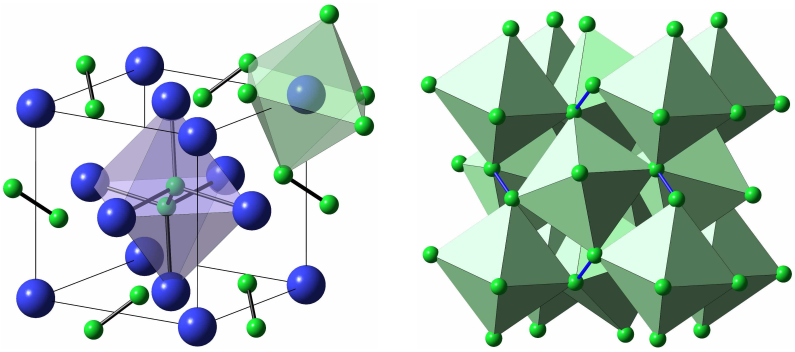

Fig. 1. Schematic unit cell of the pyrite structure PtN_2(C2). Large balls represent Pt atoms and small balls the N atoms. Each octahedral interstitial of the Pt sublattice contains one N_2 dimer. As shown in the schematic on the right side, the structure can also be regarded as a stacking of the corner-shared PtN_6 octahedra bonded with N-N connections.

The crystal structure of PtN_2(C2) is schematically shown in Fig. 1. The Pt atoms form a face-centre-cubic (FCC) sublattice. There is one N_2 dimer in each octahedral interstitial of the Pt sublattice. The N-N bonds in the N_2 dimers are parallel to the 3-fold axes of the octahedra, and each N is bonded with 3 nearest Pt atoms. Each Pt atom is octahedrally surrounded by 6 N (see Fig. 1) so that the structure can also be viewed as a stacking of corner-shared PtN_6 octahedra. It is also interesting to note that the N sublattice alone forms the α-phase of the solid nitrogen, just as the Pt sublattice adopts the FCC Pt crystalline structure.

Besides the lattice parameter *a*, the position (x, x, x) of N is the only free structural parameter of PtN_2(C2). Note that PtN_2(C2) reduces to PtN_2(C1) when x = 0.25. Fig. 2 gives the energy of PtN_2 with x varied from 0.23 to 0.42. The plot indicates that PtN_2(C1) lies at a local minimum, therefore it is a metastable structure. The lowest energy lies at x = 0.4154, corresponding to PtN_2(C2).

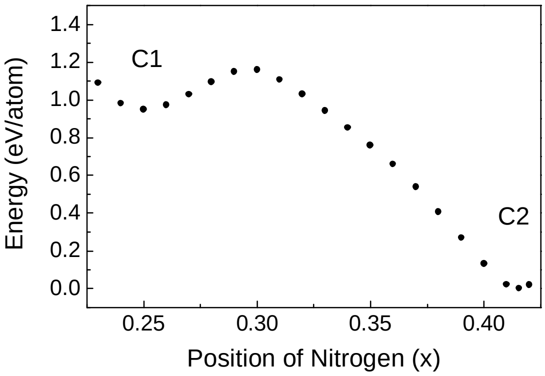

Fig. 2. Energy of PtN_2 as a function of the position of N atoms (x). When x = 0.25, PtN_2(C2) reduces to PtN_2(C1).

The calculated structural parameters and the bulk modulus of PtN_2(C2) are given in Table 1. The lattice constants (*a*) and the bulk modulus (B) were evaluated from the Vinet[19] fit to the total energies as a function of the unit cell volume. At each volume, the position of N was relaxed until the force was smaller than 0.02 eV/Å. As can be seen from Table 1, the arithmetically average lattice constant (4.816 Å) of the LDA and the

GGA values matches the experimental value (4.803 Å) very well (only 0.3 % larger). For the bulk modulus B, the LDA resulted a value of 352 GPa, well consistent with the experimental value of 354 GPa, which was obtained when the pressure dirivative B' of metal Pt (5.26) was used to fit the experimental data.[1]

Table 1. The calculated structural parameters of PtN_2(C2). The space group is Pa3 (No. 205). Pt atoms occupy 4a sites and N atoms occupy 8b sites. There are only two free parameters, i.e., the lattice constant a and the positional parameter x of nitrogen atoms. The bulk modulus B and its pressure dirivative B' are also given. In the experimental paper,[1] two pressure dirivatives were used, giving two bulk moduli.

	a (Å)	x	B (GPa)	B'
Cal. (LDA)	4.770	0.4149	352	5.20
Cal. (GGA)	4.862	0.4154	272	4.96
Exp.[1]	4.803	N/A	354/372	5.26/4

The elastic stability is a necessary condition for a crystal to exist. A cubic crystal should have following restrictions for its elastic constants[21]: $c_{44} > 0$, $c_{11} > |c_{12}|$, and $c_{11} + 2c_{12} > 0$, where c_{11}, c_{12}, and c_{44} are the elastic stiffness constants. In the present work, the elastic stiffness constants were calculated using the method described previously.[2] The calculated elastic constants are listed in Table 2. Obviously, c_{ij} fulfils the stability criteria stated above. The polycrystalline shear modulus G was calculated using the single crystal elastic constants and the Voigt-Reuss-Hill[21] averaging scheme, the obtained value (214 GPa) is 3.5 times higher than that of metal Pt (61 GPa).[22] According to the correlation between the hardness and the shear modulus,[23-24] it can be expected that PtN_2(C2) is harder than many known hard materials,[24] such as TiN, SiC, Al_2O_3, and B_4C.

Table 2. The elastic stiffness constants c_{ij}, bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio v of PtN_2(C2). All elastic constants except v are in GPa.

	c_{11}	c_{12}	c_{44}	B	G	E	v
LDA	824	117	152	352	214	535	0.247
GGA	668	78	133	272	184	452	0.226

We calculated the frequency of the high symmetry Raman mode (A_g) of PtN_2(C2) using the frozen-mode method.[25-26] The mode corresponds to a symmetric vibration of the N_2 dimers along the 3-fold axes in the cubic structure. The calculated frequency was 854 cm^{-1}, very close to the experimental value (about 860 cm^{-1} in Fig. 1 of Ref. 1). As a comparison, the calculated Raman frequency of PtN_2(C1)[5] is 628 cm^{-1}, which matches a weak peak in the Raman spectra given in Ref. 1. As indicated above, PtN_2(C1) is a metastable phase, it is likely that the coexisted PtN_2(C1) phase in experimental samples caused the observed weak Raman peak.[5]

The calculated band structure of PtN_2(C2) is shown in Fig. 3, indicating that PtN_2(C2) is a semiconductor with an indirect band gap (E_g) of 1.30 eV (GGA), or 1.77 eV (LDA). The top of the valence band locates at M, and the bottom of the conduction band locates between Γ and R. Considering that the density functional theory generally underestimates the band gap often by 30-50%, the true band gap could be a little more than 2 eV, lying in the visible region (1.65-3.1 eV) in the electromagnetic spectrum. The electronic structure of PtN_2(C2) at high pressures was also calculated and the energy gap was found to increases with pressure. At 100 GPa, the gap is 2.7 eV (GGA).

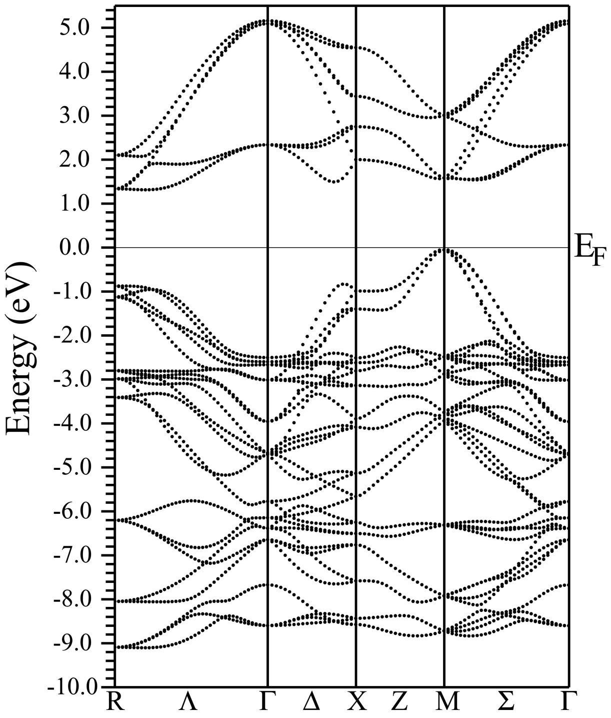

Fig. 3. Band structure of PtN_2(C2), showing an indirect band gap. The band gap E_g is 1.30 eV (GGA) or 1.77 eV (LDA).

The total density of states of PtN_2(C2) is shown in Fig. 4. The *d* states of Pt and the *p* states of N lie in the energy range between -9 eV and 0 eV (the valence band top). Their hybridation causes bonding in the PtN_6 octahedra. This is very similar to what happens in early transition metal nitrides, e.g. TiN, in which the strong metal-nonmetal bonding is formed mainly because of the *d*-*p* hybridation.[9-10]

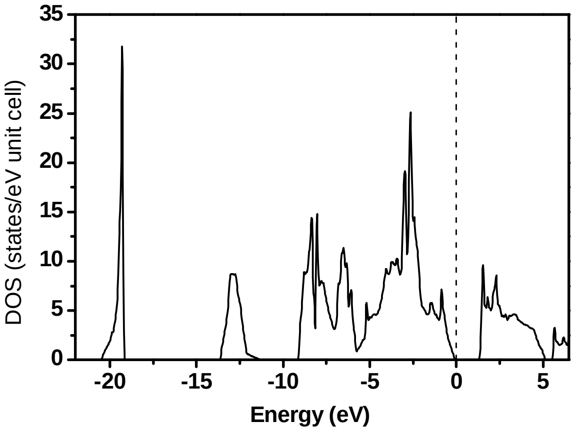

Fig. 4. Calculated total density of states (DOS) of PtN_2(C2). The valence band top locates at 0 eV.

In order to quantitatively describe the bonding in PtN_2(C2), the charge density topology was analyzed based on Bader's quantum theory of "Atoms in Molecules".[27] Table 3 lists the properties of the bonding critical points (BCP), where the electron density gradient vanishes and only one positive curvature exists, which is in the bonding direction. There are two types of BCP: One is between Pt and N, and the other is at the midpoint between the N_2 dimers. According to the topology properties at BCPs, the N-N bonding has a nature of the shared interaction because the BCP has a large electron density ρ and a negative (large in magnitude) laplacian $\nabla^2\rho$, with electronic charge concentrated in the internuclear region.[27] The properties of the N-N BCP are similar to those of the C-C bond in diamond, a well-known strong covalent bond. Therefore, the N-N bond in PtN_2(C2) is strong although it is stretched by 28% compared with the bond length in N_2 molecule. The strong N-N bonds connect the PtN_6 octahedra and the corner-shared stacking of the PtN_6 octahedra form the PtN_2(C2) structure. Apparently, the high elastic moduli of PtN_2(C2) can be attributed to the strengthening effect of the strong covalent N-N bonding.

Table 3. The bond length l, electron density ρ, and laplacian $\nabla^2\rho$ of ρ at the BCPs of PtN_2(C2) and diamond. Table shows GGA results.

BCP	l (Å)	ρ (eÅ^{-3})	$\nabla^2\rho$ (eÅ^{-5})
Pt-N	2.10	0.81	6.46
N-N	1.42	2.13	-15.78
Diamond	1.55	1.60	-15.24

In summery, the PtN_2(C2) pyrite structure, in which N_2 dimers occupy the octahedral interstitials of the Pt sublattice, was demonstrated to be elastically stable, while the phase with a fluorite structure (PtN_2(C1)) is metastable. The shear modulus of PtN_2(C2) was calculated to be 214 GPa, higher than TiN, SiC, Al_2O_3, and B_4C. In contrast to the metallic PtN_2(C1), PtN_2(C2) is semiconducting having an indirect band gap lying in the visible region in the electromagnetic spectrum. The covalent bonds between N atoms in PtN_2(C2) is quite strong, providing the main stabilizing effect for the structure.

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