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Effect of Pressure on the Electronic and Structural Properties of Platinum Nitrite (PtN) using first-principle calculations

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Abstract

Using first principle calculations within the generalized gradient approximation (GGA) the plane wave ultrasoft pseudopotential (PW-PP) and the projector – augumented wave (PAW) methods, we investigated the effect of pressure on the lattice constant, bond strength, bulk modulus and the density of state of PtN through the QUANTUM ESPRESSO package. It was found that as pressure increased from 0GPa to 50GPa, only the bond strength and bulk modulus decreased while the lattice constant volume increased with pressure and in the density of state, no energy gap was observed which indicates the metallic nature of Pt N.

1.0 Introduction

Transition metal nitrides are of great interest in both fundamental science and technical applications [1 - 9].The newly synthesized and characterized platinum nitride (PtN) [10], the first noble metal binary nitride has stimulated much theoretical research [10, 11] for its high bulk modulus and its novel electronic properties [10, 12]. In experiments, the platinum nitride was shown to have remarkably high bulk modulus of 372($\pm$5) GPa, comparable to that of cubic-BN, a known superhard material. It was shown that the Pt/N ratio is close to 1:1, with little variation given by PtN_{1-X} ($X < 0.05$); the synchrotron X-ray diffraction experiment revealed PtN to be face-centered cubic (FCC, corresponding to a zinc blende or rocksalt structure), but was unstable to distinguish between zinc blende and rocksalt due to the strong Pt signal caused by the large mass difference between Pt and N [13]. Several theoretical investigations of platinum nitride have now also been carried out, and the consensus appears to be that the compound does not crystallize in the proposed zinc-blende structure, because this arrangement would violate the requirement of positive strain energy [14 -19].

Although there exists numerous theoretical calculations on the stability, bulk modulus and electronic structures of any form of PtN, but few works focus on the effect of pressure on the structural and electronic properties of PtN using the CASTEP, VASP and WIEN2K simulation packages. In this work, we present first-principle calculations to investigate the behavior of lattice constant, bond strength, bulk modulus and the density of state of PtN under high pressure using the Quantum expresso packages.

2.0 Computational Details

We performed first-principle total energy calculations, within the generalized gradient approximation (GGA) to the density functional theory (DFT) [20]. Using the suit of codes through the QUANTUM ESPRESSO Package [21]. This work was performed using projected augmented wave pseudopotential [22], core and valence electrons are implicitly treated by ultra soft Lorenzo Paulatto-type pseudopotential as supplied by A. Dal Corso V.5.1, was generated with a sealer relativistic calculation. The interaction between II. To reduce the basis set of plane wave functions used to describe the real electronic function, ultrasoft pseudopotentials were implemented and the valences for the atomic configurations were Pt-$4f^{14}5d^{9}6s^{1}$ and N-$2S^{2}2P^{3}$. After conducting careful convergence tests it was found that an energy cutoff of 60Ry was sufficient to reduce the error, and Gaussians width of 0.02Ry was used.

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3.0 Crystal Structure

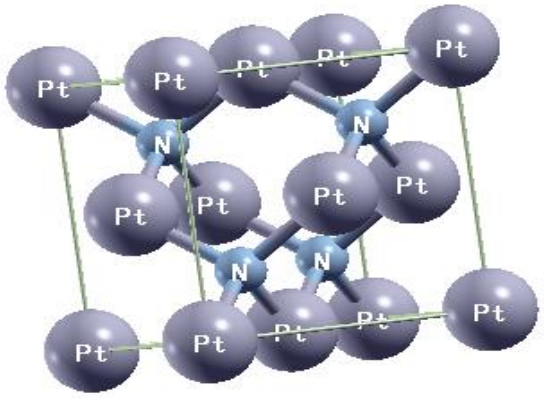

Fig.1: Zinc-blende structure of PtN.
The large atoms are Pt and the small atoms are N. only nearest neighbor bonds are represented.

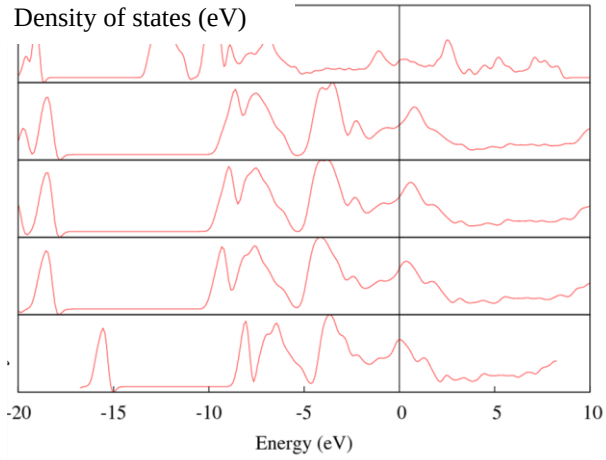

Fig. 2. Calculated total density of states (DOS) of PtN. The Fermi level at 0.

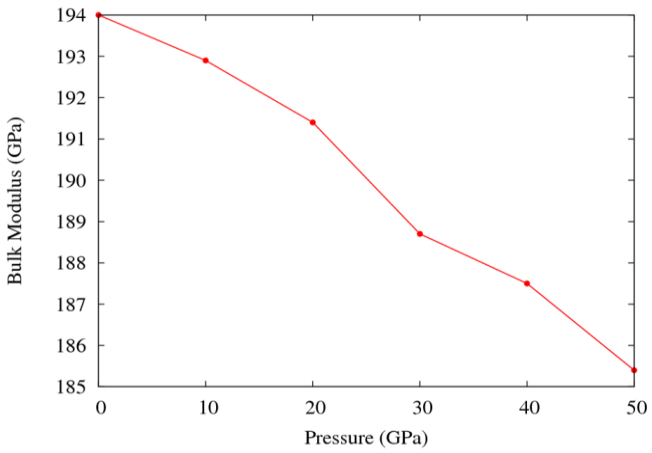

Fig. 3. The effect of pressure on the bulk modulus

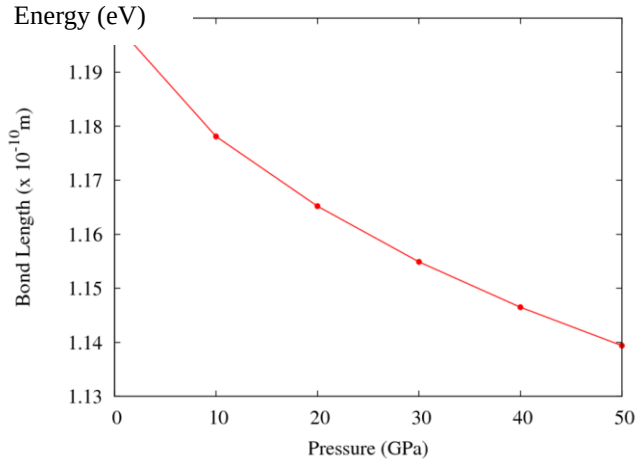

Fig. 4. The effect of pressure on the bond length of PtN.

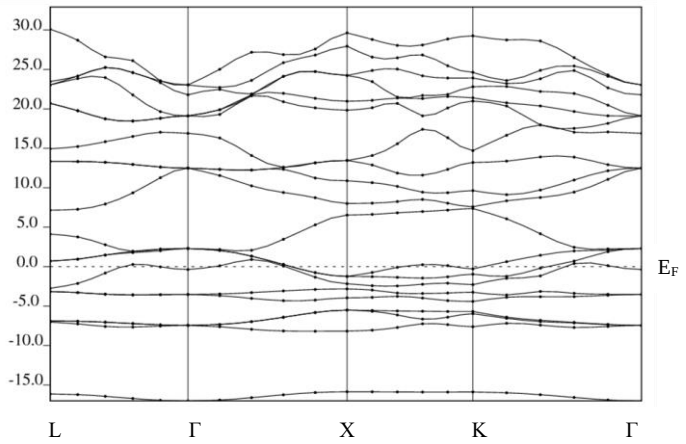

Fig. 5. Band structure of PtN.

4.0 Results and Discussions

The lattice constants a, bulk modulus B, pressure derivatives of bulk B^1, bond lengths, L of PtN under various pressure P are presented in Table 1.

Table 1:

P (GPa)	a(Å)	B(GPa)	B^1	L(Å)	$V(Å)^3$
0	9.0638	194.0	5.20	1.1991	27.58
10	9.0718	192.9	5.06	1.1781	110.63
20	9.0853	191.4	5.06	1.1652	111.13
30	9.1026	188.7	5.13	1.1549	111.76
40	9.1210	187.5	5.06	1.1465	112.44
50	9.1406	185.4	5.05	1.1394	113.17

From the Birch-Murnaghan fit to the total energies as a function of the unit cell volume, the lattice constants (a), the bulk modulus(B) and the pressure derivatives (B^1) were evaluated as shown in table 1. According to the Murnaghan equation of state, the bulk modulus will be doubled if the volume used in the calculation is half the real volume [23]. for the cubic PtN, there is one platinum atom and one nitrogen atom per primitive cell.

Fig. 2 represents the electronic structures of PtN at various pressures ranging from 0GPa to 50GPa. This total density of states (DOS) shows a shift of diminishing peaks beyond the Fermi level as the pressure increases.

From Fig. 3, we observed a reduction in the values of the bulk modulus as the pressure increases from 0GPa to 50GPa, which is a clear indication that increase in pressure weakens the strength or stiffness of the material. And Fig. 4 represents the effect of pressure on the bond length of PtN, it shows that increase in pressure reduces the inter-atomic distance.

Fig. 5 represents the band structure of PtN along high symmetry points calculated using generalized gradient approximation (GGA) with Fermi energy level E_F taken at 0 eV as shown by the dotted lines. The self-consistence calculations were performed using the plane wave ultrasoft pseudopotential (PW-PP) and the projector – augumented wave (PAW) methods with the theoretical lattice constant (a) given in Table 1.

CONCLUSION

Using the first-principle calculations we have computed electronic and structural properties of PtN under high pressures. In summary, we observed that increase in pressure leads to increase in the lattice constants and volume, and a reduction in the bulk modulus and the bond lengths of the material.

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