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Electronic properties of the binary noble metal nitride PtN: First-principles calculations

M. B. Kanoun*
Unité de Recherche-Matériaux et Energies Renouvelables, Département de Physique, Faculté des Sciences, Université A. Belkaid, Tlemcen, Boîte Postale 119, 13000 Tlemcen, Algeria

S. Goumri-Said†
Condensed Matter Theory Group, Department of Physics, Kaiserslautern University of Technology, Box 3049, D-67653 Kaiserslautern, Germany

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This paper is devoted to the first-principles calculations of electronic properties of the recently synthesized noble metal nitride (PtN) [E. Gregoryanz *et al.*, Nature Material **3**, 294 (2004)]. We report in this work the band structure, and total and partial densities of states, which show the metal character of PtN. These results indicate that there is a strong hybridization between the N(p) states and the Pt(d) states with the energy position. The bonding character of PtN is determined by two competitive processes: a loss in metal-metal bond strength and a gain in energy due to favorable bonding interactions with the Pt atom.

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From a technology point of view, materials based on nitrogen are very interesting and offer different advantages. Under normal conditions, nitrogen is stable and may react with selected elements to form different compounds with interesting properties.[1] Nitrides (in particular, group III and IV elements) are used in numerous applications such as optoelectronic (light-emitting diodes and semiconducting lasers). Among the group III elements that form nitrides, AlN and GaN have already attracted much of our attention since 2003,[2–5] and we have covered their physical, structural, and electronic properties using different theoretical methods.

Another important group of these materials formed by transition metals (e.g., Zr, V, and Mo) are nitrides mostly known for their superconducting properties.[6,7] Most of these transition metals can form stable nitrides at high temperatures and at either ambient or high pressure. There are other groups for which there are no known binary nitride compounds, such as those in the nickel and copper groups (for example, Cu, Au, or Ag). Because of their structural simplicity and stability, most of these metals are used as pressure standards in diamond-anvil-cell experiments, with platinum probably being the most often used.[8] Until 2004 Pt was not known to form a nitride. The synthesis of this new nitride at pressures up to 50 GPa, using laser-heated diamond-anvil-cell techniques, has been successfully performed by E. Gregoryanz *et al.*[9] This work has important implications for high-pressure experiments and technology, namely, the possibility to synthesize other nitrides with transition metals, and has suggested us the performance of the present theoretical study of this compound.

To investigate the electronic properties of PtN, we apply the hybrid full-potential (linearized) augmented plane-wave plus local orbitals (FP-L/APW+lo)[10] method within the density functional theory (DFT), where the electrons exchange-correlation energy is described with a local density approximation (LDA), for which we adopt the Ceperley-Alder forms and parametrization of Perdew and Wang.[11,12] The new approach APW+lo is shown to reproduce the accurate results of the LAPW method, but using a smaller basis set size. Due to the smaller basis set and faster matrix setup, APW+lo offers a shorter run time and uses less memory than LAPW. Moreover, the use of APW+lo is more suitable for calculations with a large ratio of basis functions to atoms (e.g., for open crystal structures, surfaces, and molecules on surfaces).[13,14] In the FP-L/APW+lo method, one employs Slaters' old idea of muffin-tin approximation to divide the space into two regions. Near the atoms, all quantities of interest are expanded in spherical harmonics and in the interstitial region they are expanded in plane waves. The first type of expansion is defined within a so-called muffin-tin sphere of radius, RMT, around each nucleus. In our work, a fully relativistic calculation[15] was performed for core states (without spin-orbital effects), whereas the valence states were treated in a scalar relativistic scheme. The maximum value l for the wave-function expansion inside the atomic spheres is confined to $l_{max}=10$, the wave functions is expanded in plane waves with a cutoff of $K_{MAX}=8/R_{MT}$ [K_{MAX} is the maximum modulus for the reciprocal lattice vector, and R_{MT} is the average radius of the muffin-tin (MT) spheres]. Then we chose

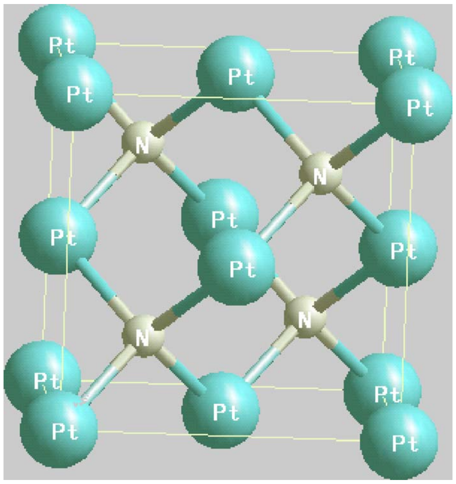

FIG. 1. (Color online) Zinc-blende PtN structure.

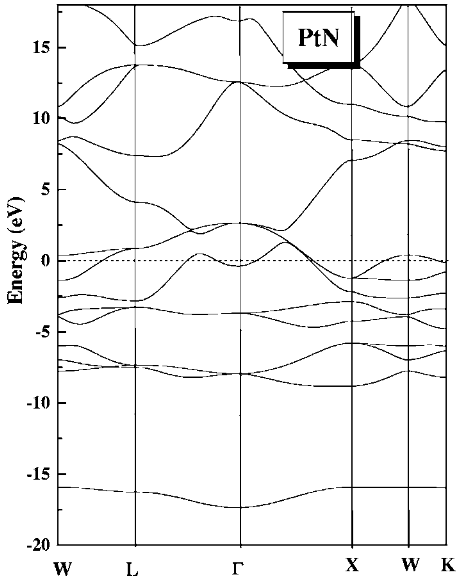

FIG. 2. Band structure along the principal high-symmetry directions in the Brillouin zone of zinc-blende PtN.

the plane-wave basis set for the remaining space of the unit cell. For MT radius, we adopt the following values: 1.9 Bohr for Pt and 1.65 Bohr for N. The *k* integration over the Brillouin zone is performed using Monkhorst and Pack.[16] The total and partial densities of states (DOS) were obtained using a modified tetrahedron method of Blochl *et al.*[17] A mesh yielded 500 *k* points in the irreducible wedge of the Brillouin zone. The iteration process is repeated until the calculated total energy of the crystal converges to less than 1 mRy.

As a first step of our calculations, we minimize the total energy versus volume curve to determine the structural parameters of zinc-blende PtN (Fig. 1). The use of Murnaghan's equation of state[18] allows us to calculate the lattice constant: $a=4.69$ Å, which is slightly smaller than the experimental value $a=4.80$ Å.[9,19]

The electronic band structures of zinc-blende PtN along symmetry lines are displayed in Fig. 2. No energy gap is seen, which indicates the metallic nature of platinum nitride. Characteristic band separations can be determined by E_{Ns-Np} (i.e., energy gap between the *Ns* band and the valence band complex), which is equal to 8.571 eV. We also calculated the zone-center metal *d* band splitting, ΔE_d, which is equal to 2.05 eV, and E_p-E_s is the $(Np-Ns)$ energy gap, $E(\Gamma_{15}) - E(\Gamma_1)$, and is equal to 20.04 eV.

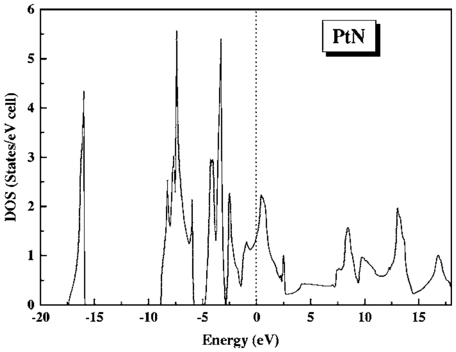

FIG. 3. Calculated total density of states (DOS) in zinc-blende PtN.

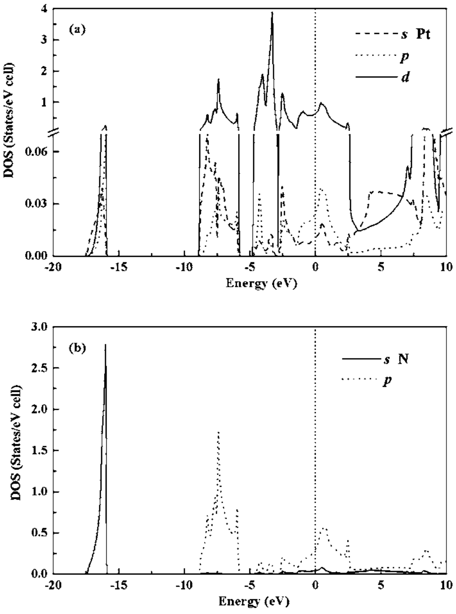

FIG. 4. The angular momentum decomposition of the atom-projected densities of states in PtN. (a) Pt *s*, *p*, and *d* states and (b) N *s* and *p* states.

From the calculated total DOS shown in Fig. 3, we can clearly extract the location of the different subbands, which are shown in the electronic band structure. The states between −17.5 and −16 eV are dominated by N (2*s*) states with a small contribution from Pt. The states above −9 eV are mainly composed of Pt (5*d*) and N (2*p*) orbitals. The *s*, *p*, and *d* components of the density of states within the Pt and N MT spheres for the zinc-blende PtN are shown in Fig. 4. These results indicate that there is a strong hybridization between the N states and the Pt states with the energy position. The feature lying lowest in energy is the N 2*s* derived state. With respect to the valence band, we observe two high density regions separated by a low electron density region. The upper region is mainly due to Pt *d* states with some N *p* component. Also the N *s* state mixes with the Pt *s* states.

In order to visualize the nature of the bond's character and to explain the charge transfer in PtN, we calculate the total

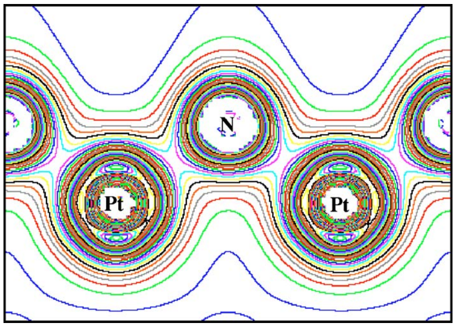

FIG. 5. (Color online) Total valence charge density plots for zinc-blende PtN in the (110) plane.

charge density. The total valence charge density is displayed in the (110) plane containing Pt and N (see Fig. 5). The PtN compound involves the bonding of transition metal to non-transition metal. This bonding can be conceived by two competitive processes:[20] (i) a loss in metal-metal bond strength due to the (usual) enlargement of the unit cell volume caused by the addition of N in the interstitial positions of the fcc lattice, and (ii) an energy gain due to favorable bonding interactions with the Pt atom. In Fig. 5, one can see that there is an increase in electron density at the N atoms and a decrease in the interstitial region between the metal atoms where the metal-metal bonding was formed in the reference structure. We conclude that this charge rearrangement reflects the electronegative nature of N. There is also a decrease of electron density at the metal atoms. One can see clearly that the bonding charge is displaced strongly from the midpoint between the Pt atom towards the N atom. The displacement of the bonding charge listed above increases as the difference between the electronegativity values of the two atoms Pt and N increases.

In summary, the electronic and bonding properties of zinc-blende platinum nitride has been investigated using first-principles calculations. It is found that PtN is the first transition metal zinc-blende crystal. Also we have found an ionic component with a significant charge transfer to the more electronegative nitrogen atom, as well as clearly a metallic nature. The present study constitutes a first step, which will hopefully stimulate other theoretical predictive investigations of metal transition nitrides not yet synthesized, with an aim to complete future experimental works.

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*Electronic address: m_kanoun@mail.univ-tlemcen.dz

†Electronic address: sgoumri@physik.uni-kl.de

[1] P. E. McMilian, Nat. Mater. **1**, 19 (2003).

[2] M. B. Kanoun, S. Goumri-Said, A. E. Merad, G. Merad, J. Cibert, and H. Aourag, Semicond. Sci. Technol. **19**, 1220 (2004).

[3] M. B. Kanoun, A. E. Merad, J. Cibert, H. Aourag, and G. Merad, J. Alloys Compd. **366**, 86 (2004); Solid-State Electron. **48**, 1601 (2004).

[4] A. E. Merad, M. B. Kanoun, J. Cibert, H. Aourag, and G. Merad, Mater. Chem. Phys. **82**, 471 (2003).

[5] S. Goumri-Said, M. B. Kanoun, A. E. Merad, G. Merad, and H. Aourag, Chem. Phys. **302**, 135 (2004).

[6] N. Pessal, R. E. Gold, and W. A. Reichardt, J. Phys. Chem. Solids **29**, 19 (1968).

[7] T. Takamori, K. Shih, D. B. Dove, R. W. Nywening, and M. E. Re, J. Appl. Phys. **68**, 2191 (1990).

[8] N. C. Holmes, J. A. Moriarty, G. R. Gathers, and W. J. Nellis, J. Appl. Phys. **66**, 2962 (1989).

[9] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H. K. Mao, and R. J. Hemley, Nat. Mater. **3**, 294 (2004).

[10] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, An Augmented-Plane-Wave+Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn Wien, Austria, 2001).

[11] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[12] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[13] E. Sjostedt, L. Nordstrom, and D. J. Singh, Solid State Commun. **114**, 15 (2000).

[14] G. K. H. Madsen, P. Blaha, K. Schwarz, E. Sjostedt, and L. Nordstrom, Phys. Rev. B **64**, 195134 (2001).

[15] D. D. Koelling and B. N. Harmon, J. Phys. C **10**, 3107 (1977).

[16] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[17] P. E. Blochl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).

[18] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[19] This understimation is due to essentially to the overbinding tendency within DFT and LDA but it does not affect the calculation of the other quantities.

[20] C. D. Gelatt Jr., A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **27**, 2005 (1983).