Semiconducting (Half-Metallic) Ferromagnetism in Mn(Fe) Substituted Pt and Pd Nitrides

Abdesalem Houari
Laboratoire de Physique Théorique, Département de Physique, Université de Béjaia, Béjaia, Algérie

Samir F. Matar
CNRS, Université de Bordeaux, ICMCB, 87 avenue du Docteur Albert Schweitzer, 33600 Pessac, France

Volker Eyert
Center for Electronic Correlations and Magnetism,
Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany

(Dated: January 11, 2011)

Using first principles calculations as based on density functional theory, we propose a class of so far unexplored diluted ferromagnetic semiconductors and half-metals. Here, we study the electronic properties of recently synthesized 4d and 5d transition metal dinitrides. In particular, we address Mn- and Fe-substitution in PtN$_2$ and PdN$_2$. Structural relaxation shows that the resulting ordered compounds, Pt$_{0.75}$(Mn,Fe)$_{0.25}$N$_2$ and Pd$_{0.75}$(Mn,Fe)$_{0.25}$N$_2$, maintain the cubic crystal symmetry of the parent compounds. On substitution, all compounds exhibit long-range ferromagnetic order. While both Pt$_{0.75}$Mn$_{0.25}$N$_2$ and Pd$_{0.75}$Mn$_{0.25}$N$_2$ are semiconducting, Fe-substitution causes half-metallic behavior for both parent materials.

PACS numbers: 71.15.Mb, 71.15.Nc, 71.20-b, 75.10.Lp, 75.25.Ha, 73.43.Cd

Keywords:

Being known since the beginning of the 20th century, transition metal nitrides are considered as an exciting class of materials due to a wide range of technological applications. Traditionally, the great advantages of these compounds concern their hardness and refractory nature. However, much attention is currently directed towards their electronic, magnetic, and optical properties, where fascinating applications are expected. Many efforts, experimental as well as theoretical, have been made to study the transition metal nitrides. Until recently none of the noble metal nitrides or the platinum group nitrides were known. The first synthesis of platinum nitride (Pt-N), under extreme conditions of pressure and temperature, was reported only few years ago. Lateron, several other nitrides of different elements (Ir, Os, Ru and Pd) were also obtained.

There was a debate about the crystal structure and the stoichiometry of platinum nitride. While a zinc-blende structure was first proposed, Crowhurst et al. demonstrated that this nitride crystallizes neither in zinc-blende (PtN: mononitride) nor in fluorite (PtN$_2$: dinitride) type structures, which are highly unstable at the synthesis conditions ($P = 50$ GPa and $T = 2000$ K). Instead, the authors revealed that the compound is a dinitride, hence PtN$_2$, and the ground state structure is a cubic pyrite structure. Lateron, these authors succeeded in synthesizing IrN$_2$ and PdN$_2$, where the first one is found to be in the monoclinic baddeleyite structure. Yet, PdN$_2$, which could by synthesized at high pressures but was not stable at ambient conditions, was proposed to also crystallize in the pyrite structure. In a recent theoretical investigation it was shown that tetragonal distortions may stabilize PdN$_2$ at ambient pressure. Other nitrides (OsN$_2$, RuN$_2$ and RhN$_2$) have been also obtained and are shown to crystallize in marcasite type structure.

Platinum dinitride has been predicted to have excellent mechanical properties. The calculated hardness (bulk modulus, shear modulus and other elastic constants) shows that it is harder than many known hard materials like TiN and SiC. The electronic properties of PtN$_2$ are also very interesting. Contrary to other transition metal nitrides, which are almost all metallic, PtN$_2$ is found to be semiconducting, and this could make it an important material for optoelectronic applications. Band structure calculations as based on density functional theory and the local density approximation (LDA) show an indirect band gap of $\sim 1.5$ eV, which is probably somewhat smaller than the experimental value due to the tendency of the LDA to underestimate the band gap.
range ferromagnetic order. In contrast, NiS₂ is an antiferromagnetic insulator, where the insulating behaviour has been attributed to the presence of strong electronic correlations.

Our present work is focused especially on the electronic and magnetic properties of substituted PtN₂ and PdN₂. We demonstrate that substitution of the non-magnetic 4d- and 5d-transition metal ions by the magnetic 3d-ions Mn and Fe may lead to semiconducting and half-metallic ferromagnetism, respectively.

In our investigation, we first consider Mn-substitution in PtN₂ and PdN₂. For the latter compound, we assumed a cubic pyrite crystal structure as for PtN₂. This assumption is based on the fact that experimentally PdN₂ is actually synthesized in cubic pyrite structure at high pressure conditions, even though it is not stable at ambient pressure. Replacing one of the four Pt and Pd by magnetic Mn leads to Pt₀.₇₅Mn₀.₂₅N₂ and Pd₀.₇₅Mn₀.₂₅N₂, respectively. To check if the cubic symmetry is maintained on Mn-substitution, a quantum molecular dynamics relaxation has been performed using the Siesta ab initio simulation package with norm-conserving pseudopotentials. Both atomic positions and cell shape were included in the relaxation process. As a result, neither Pt₀.₇₅Mn₀.₂₅N₂ nor Pd₀.₇₅Mn₀.₂₅N₂ display any deviations from cubic symmetry and the atoms remain nearly at the positions of the pure compound. In particular, the internal nitrogen parameters are almost unchanged after Mn-substitution in both PtN₂ and PdN₂. The changes in the nitrogen positions are within 0.07 Å. To be specific, in PtN₂ the internal nitrogen parameter changes from 0.415 (as given in Ref. 8) to 0.416 after the relaxation of the substituted system.

In a second step, full potential augmented spherical wave (FPASW) calculations were carried out in order to address the electronic properties of all compounds under study. To start with, we recalculated the equilibrium lattice constant. From non-spin polarized LDA calculations, we obtained a lattice parameter of a₁₁ = 4.79 Å for Pt₀.₇₅Mn₀.₂₅N₂. Taking into account spin polarization led to a slightly larger value of a₁₁ = 4.82 Å, with the ferromagnetic state being more stable than the non-magnetic one. It is important to note that the values obtained for the lattice constant of Pt₀.₇₅Mn₀.₂₅N₂ resemble that of PtN₂, which is a = 4.80 Å, and confirm the molecular dynamics result. To conclude from both sets of calculations, not only the cubic symmetry is preserved after Mn-substitution, but even the lattice constant is almost not affected. The negligible changes of the structure can be understood from the fact that only one out of four Pt atoms is replaced and thus the platinum network is affected by the substitution only to a small degree. Motivated by these findings, we decided to perform the calculations for Pd₀.₇₅Mn₀.₂₅N₂ using the same lattice constant as for PdN₂, i.e. a = 4.75 Å (see also the discussion below).

Subsequently, the electronic structures of the Mn-substituted compounds were analyzed in terms of the projected densities of states as arising from the FPASW calculations. However, for the Mn-substituted systems the LDA results bear some ambiguity. To be specific, we obtain semiconducting behavior for Pd₀.₇₅Mn₀.₂₅N₂, whereas Pt₀.₇₅Mn₀.₂₅N₂ is at the verge of being a semiconductor but displays a small band overlap. In order to check these findings, we additionally performed a set of calculations based on the GGA. They resulted in semiconducting ferromagnetic ground states for both compounds with indirect band gaps of 0.17 eV and 0.42 eV for Pt₀.₇₅Mn₀.₂₅N₂ and Pd₀.₇₅Mn₀.₂₅N₂, respectively. The corresponding partial densities of states (DOS) are illustrated in Figs. 1 and 2. The spectrum falls essentially in four parts. While the low-energy range from −9 to −6 eV and from −8 to −4 eV for Pt₀.₇₅Mn₀.₂₅N₂ and Pd₀.₇₅Mn₀.₂₅N₂, respectively, is dominated by the N 2p states, the upper valence band is formed mainly by the t₂g manifolds of the transition metal d states. For the
spin-minority bands, the situation is slightly more complicated. Whereas the Pd 4d and Pt 5d states are fully occupied and found in the same energy range as their spin-majority counterparts, the Mn 3d $t_{2g}$ states experience strong exchange splitting. As a result, the Mn 3d $t_{2g}$ spin-down states form the lower conduction band of this spin channel and a magnetic moment of $3\mu_B$ is found at these atoms. In contrast, spin polarizations of Pd, Pt, and N are negligible. Finally, the remaining conduction band states can be attributed to the transition metal d states of $e_g$ symmetry. Since the latter form $\sigma$-type bonds with the N 2p states, we find a considerable admixture of both types of states in the lower valence and upper conduction band. This admixture is much smaller for the bands between $-6$ and $+1$ eV and $-4$ to $+2$ eV, respectively, which are of $t_{2g}$ symmetry and form less strong $\pi$ bonds. In passing we mention the albeit small band gaps, which make both Mn-substituted compounds semiconducting.

In order to check this, we performed additional GGA+U calculations for Pt$_{0.75}$Mn$_{0.25}$N$_2$. While there were no qualitative changes, both the exchange splitting of the Mn 3d $t_{2g}$ states and the optical band gap increased considerably.

The second substitution that we considered was the replacement of Pt and Pd by iron, leading to the ordered compounds Pt$_{0.75}$Fe$_{0.25}$N$_2$ and Pd$_{0.75}$Fe$_{0.25}$N$_2$. Our procedure was the same as for Mn-substitution. Molecular dynamics relaxations using the Siesta code (with the same calculations details cited above) were performed including relaxation of both the atomic positions and the cell shape. As in the Mn-case we found that the cubic symmetry is not broken on Fe-substitution and that even the internal nitrogen parameter remained essentially unchanged.

For the FPASW calculations performed in a second step in order to address the electronic and magnetic properties, we followed the procedure already adopted for PdN$_2$ and used the lattice constants of the pure systems also for the substituted materials. In this case, our procedure was justified by an additional recalculation of the equilibrium lattice constant for Pd$_{0.75}$Fe$_{0.25}$N$_2$. As a result, values of $a_{\chi M} = 4.742\ \text{Å}$ and $a_{FM} = 4.749\ \text{Å}$ were obtained as arising from non-spin polarized and spin polarized calculations, respectively. The latter value is almost identical to the value of $a = 4.75\ \text{Å}$ of pure PdN$_2$.

Again, the LDA results bear some ambiguity as they led to half-metallic behavior for Pd$_{0.75}$Fe$_{0.25}$N$_2$ but metallicity of both spin channels for Pt$_{0.75}$Fe$_{0.25}$N$_2$. Yet, the spin-majority density of states at the Fermi energy was found to be very small. The problem could again be resolved by GGA calculations, which render both substituted materials half-metallic. Both compounds exhibit stable magnetic order with magnetic moments of $2.0\ \mu_B$ located almost completely at the iron atoms.

The electronic structure and partial DOS of the two compounds as arising from the spin-polarized ferromagnetic calculations are illustrated in Figs. 3 and 4. The gross features of the partial densities of states are the same as for the Mn-substituted compounds. Differences are due to the smaller magnetic moments of the Fe atoms, which lead to reduced exchange splittings of the 3d $t_{2g}$ states. As a consequence, the respective spin-majority bands are shifted to higher energies as compared to the d states of the Pt and Pd matrix. In addition, the Fe spin-minority bands are shifted to lower energies as compared to the Mn-systems due to the increased electron count. As a result, the semiconducting behavior is lost and a metallic spin-down channel found. Again, these results were qualitatively confirmed by additional GGA+U calculations, which revealed an increase of the exchange splitting of the Fe 3d $t_{2g}$ states as well as the band gap of the spin-majority channel.

In passing, we mention additional spin polarized calculations, which were performed Pt$_{0.75}$Mn$_{0.25}$N$_2$ in order to check for long range antiferromagnetic order. For these calculations, we used a tetragonal structure arising from...
doubling the cubic cell along the c axis. As a result, an antiferromagnetic and again semiconducting solution was found albeit with a total energy, which by about 7 mRy/f.u. higher than that of the ferromagnetic ground state.

In summary, based on our first principles investigation we propose the existence of so far unexplored diluted ferromagnetic semiconductors and half-metals. These materials arise from substituting magnetic 3d ions (Mn, Fe) in the non-magnetic dinitrides PtN$_2$ and PdN$_2$. According to molecular dynamics calculations, the ordered compounds A$_{0.75}$B$_{0.25}$N$_2$, where A = Pt, Pd and B = Mn, Fe, preserve the cubic pyrite structure of their parent compounds. On substitution, stable long-range ferromagnetic order results with magnetic moments of 3$\mu_B$ and 2$\mu_B$, which are well localized at the Mn- and Fe-sites, respectively. While Mn-substitution leads to semiconducting behavior, introduction of iron causes the substituted compounds to be half-metallic. Our results still await experimental confirmation.

**Acknowledgments**

This work was supported by the Deutsche Forschungsgemeinschaft through TRR 80.

---

* Corresponding authors: 
  [habdslam@yahoo.fr](mailto:habdslam@yahoo.fr) 
  [volker@eyert.de](mailto:volker@eyert.de)

1. S. T. Oyama, *Introduction to the chemistry of transition metal carbides and nitrides*, in: The chemistry of Transition Metal Carbides and Nitrides, edited by S. T. Oyama (Blackie Academic & Professional, London 1996), Chap. 1.
2. H. O. Pierson, *Handbook of Refractory Carbides and Nitrides* (Noyes Publications, Westwood 1996), Chaps. 9-13.
3. A. Houari, S. F. Matar, M. A. Belkhir, and M. Nakhl, Phys. Rev. B 75, 064420 (2007).
4. A. Houari, S. F. Matar, and M. A. Belkhir, Computational Material. Science 43, 392 (2008).
5. S. Jhi, J. Ihm, S. G. Louis, and M. L. Cohen, Nature 399, 132 (1999).
6. U. Lundin, L. Fast, L. Nordstrom, B. Johansson, J. M. Wills, and O. Eriksson, Phys. Rev. B 57, 4979 (1998).
7. E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H. K. Mao, and R. J. Hemley, Nat. Mater. 3, 294 (2004).
8. J. C. Crowhurst, A. F. Goncharov, B. Sadigh, C. L. Evans, P. G. Morrall, J. L. Ferreira, and A. J. Nelson, Science 311, 1275 (2006).
9. J. C. Crowhurst A. F. Goncharov, B. Sadigh, J. M. Zaug, D. Abegg, Y. Meng, V. B. Prakapenka, J. Mater. Res. 23, 1 (2008).
10. A. F. Young, C. Sanloup, E. Gregoryanz, S. Scandolo, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. 96, 155501 (2006).
11. R. Yu, Q. Zhan, and L. C. De Jonghe, Inorg. Chem. Int. Ed. 46, 1136 (2007).
12. D. Abegg, B. Sadigh, J. C. Crowhurst and A. F. Goncharov, Phys. Rev. Lett. 100, 095501 (2008).
13. R. Yu, Q. Zhan and X. F. Zhang, Appl. Phys. Lett. 88, 051913 (2006).
14. H. Gou, L. Hou, J. Zhang, G. Sun, L. Gao and F. Gao, Appl. Phys. Lett. 89, 141910 (2006).
15. A. F. Young, J.A. Montoya, C. Sanloup, M. Lazzeri, E. Gregoryanz, and S. Scandolo, Phys. Rev. B 73, 153102 (2006).
16. R. Weirich, S. F. Matar, E. Betranhandy, and V. Eyert, Solid State Sciences 5, 701 (2003).
17. R. Weirich, V. Eyert, and S. F. Matar, Chem. Phys. Lett. 373, 636 (2003).
18. J. B. Goodenough, J. Solid State Chem. 3, 26 (1971).
19. V. Eyert, K.-H. Höck, S. Fiechter, and H. Tributsch, Phys. Rev. B 57, 6350 (1998).
20. K. Bürker, S. Fiechter, V. Eyert, and H. Tributsch, J. Electrochem. Soc. 146, 261 (1999).
21. J. M. Soler, J. D. Gale, A. García, J. Junquera, P. Ordejon, D. Sanchez-Portal, J. Phys: Cond. Matter 14, 2747 (2002).
22. N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
23. V. Eyert, Int. J. Quantum Chem. 77, 1007 (2000).
24. V. Eyert, *The Augmented Spherical Wave Method – A Comprehensive Treatment*, Lect. Notes Phys. 719 (Springer, Heidelberg, 2007).
25. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).