Structural, electronic and magnetic properties of zinc-blende Ga 1-x TMx N (TM = Cr, Mn, Fe, V)

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REVIEW PAPER

Structural, Electronic and Magnetic Properties of Zinc-Blende $Ga_{1-x}TM_xN$ (TM = Cr, Mn, Fe, V)

F. Dahmane · A. Tadjer · B. Doumi · D. Mesri · H. Aourag

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Abstract In this paper, we present a theoretical study of structural, electronic and magnetic properties for zinc-blende $Ga_{1-x}TM_xN$(TM = Cr, Fe, Mn, V) using the full-potential augmented plane wave (FP-APW) method with local-spin density approximation (LSDA). We have analysed the dependence of structural parameters values on the composition x in the range of $x = 0.25$, $x = 0.50$. Also, the role of p–d hybridisation is analysed by partial (PDOS) and total density of states (TDOS). The magnetic moment of $Ga_{1-x}TM_xN$ has been studied by increasing the concentration of TM atom. The TM atom is the most important source of the total magnetic moment in these alloys, while the contributions from Ga and N are minor. In addition our results verify the half-metallic ferromagnetic character of TM doped GaN.

Keywords First-principales calculations · Diluted magnetic semiconductor · GaN · Transition metals · Magnetic moment

1 Introduction

The study for magnetic materials with optimised optical, electronic, structural and magnetic properties has attracted much attention. Wide band-gap semiconducting binary nitrides such as GaN, AlN, InN, BN, are currently being intensively investigated worldwide. The large interest originates from their promising potential for short-wavelength light-emitting diodes, semiconductor lasers and optical detectors, as well as for high-temperature, high-power and high-frequency devices [1]. These materials, besides being a prime object of interest of device engineers, are also an exciting subject of research for a physicist. This is because of their outstanding position in the III–V family of semiconductors. GaN, InN and AlN, unlike other III–V materials are hard, partially ionic semiconductor compounds of high chemical and thermal stability [2]. The magnetic property in dilute magnetic semiconductors (DMS) emerges from an interaction between the localised spin-polarised d-electrons of the transition-metal impurities with the delocalised carriers (electrons) in the host semiconductor [3]. Scientists have focussed on developing new semiconductor spintronic devices. Spintronic applications use both the electrical charge and the spin of electrons to increase considerably the functionality of devices designed with conventional semiconductors [4]. Group III-nitrides crystallise in zinc-blende (ZB) and wurtzite (WZ) structures. The space group of ZB structure nitrides is F-43m and contains four molecules in its unit cube like that of zinc sulfide and is developed on a face-centred lattice.

Among the group-III nitrides GaN is currently actively investigated in view of its promising potential for development of short-wave length optoelectronic devices. Under ambient conditions GaN crystallises in the hexagonal wurtzite structure with the space group C_{6v}^4. However, the epitaxy of thin GaN films [5–7] has been demonstrated also to result in the cubic zincblende structure with the space group T_d^2. Typical total energy differences between WZ and ZB GaN are known to be very small (fractions of

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mRy/atom) both experimentally and theoretically [8]. GaN exhibits some unique properties, such as a large band gap and strong interatomic bond [5]. The possibility of making it ferromagnetic by injecting into it spin-polarised electrons from a 3d transition metal further increases its potential for spintronics applications.

Transition metal are a very interesting class of materials, because they have unique properties such as high hardness, brittleness, high melting temperature, good electrical-thermal conductivity and superconductivity [9]. Due to their hardness, high melting points, high stability and good wear and corrosion resistance, transition metals are generally used in industry. Because of their particular electronic structure they show a remarkable combination of ionic, covalent and metallic properties. The gallium nitride doped by transition metals belongs to a class of dilute magnetic semiconductors which have been recently explored as potential candidates for spintronic applications [10]. In this work we report the first theoretical study of the electronic structure and magnetism of TM doped GaN.

2 Method of Calculation

The structural, electronic and magnetic properties of $Ga_{1-x}TM_xN$ (TM = V, Fe, Mn, Cr) may be investigated using total energy and electronic structure calculations based on the local-spin density approximation (LSDA) to density-functional theory. The electronic configuration for GaN is Ga: Ar $3d^{10}4s^24p^1$, N:He $2s^22p^3$, and the electronic configuration of TM are V:Ar $4s^23d^3$, Cr: Ar $4s^13d^5$ Mn: Ar $4s^23d^5$,and Fe: Ar $4s^23d^6$. For the electronic configuration of TM ions we use: V^{3+}: Ar $3d^2$ (with two electrons at eg state), Cr^{+3}: Ar $3d^3$(with two electrons at eg state and one electron at t2g state), Mn^{+3}: Ar $3d^4$ (with two electrons at eg and two electrons at t2g) and Fe^{+3}: Ar $3d^5$ (with two electrons at eg state and three electrons at t2g).

We have used an approximation for the calculation of exchange-correlation energy functional, that is, the standard local density approximation (LDA), as implemented in the WIEN2K code [11]. In order to achieve convergence of the energy eigenvalues, the wave functions in the interstitial region were expanded in plane waves with a cut-off of $k_{\max} = 8/\text{RMT}$ (where RMT is the average radius of the MT spheres). A mesh of 64 special k-points is taken in the irreducible wedge of the Brillouin zone (IBZ). The RMT values for GaN are assumed to be 1.74 and 1.62 a.u. for Ga and N, respectively. The GaN has zinc blende structure with space group F-43m in which the Ga atom is located at (0, 0, 0) and N atom at (0.25, 0.25, 0.25). When TM is doped with concentration $x = 0.25$, the calculations are formed with an eight-atom supercell, constructed by taking $1 \times 1 \times 1$ standard unit cell of structure with cubic symmetry belong to space group P-43m. In the eight-atom supercell, we replace one Ga atom at (0, 0, 0) by TM. For $x = 0.5$, we replace two Ga atoms by TM. The iteration process was repeated until the calculated total energy of the crystal converged to less than 10^{-4} Ryd.

3 Results and Discussions

3.1 Structural Properties

An important question is how the structural electronic and the magnetic properties of semiconductors alloys change as a function of composition x. In order to study these properties of the ternary $Ga_{1-x}TM_xN$ alloys at compositions $x = 0, 0.25, 0.50$, we first calculate the structural properties of the binary compound GaN. For all composition of $Ga_{1-x}TM_xN$ structural optimisation is performed by minimising the total energy with respect to the unit cell volume using Murnaghan's equation of state [12]. The lattice constant a, the bulk modulus B and first order pressure derivative of the bulk modulus B', for different concentrations of TM in GaN are displayed in Table 1. It is well-known that the structural parameters vary with composition in conventional semiconductor alloys. The variation in the lattice parameter follows Vegard's law, however, this is not a case for semiconductor alloys having strong difference of electronegativity and size of atoms. The physical properties show strong deviation from a simple linear variation. In these systems, the differences from Vegard's law are generally weak. C. Caetano et al. [13] have pointed out that Vegard's law is not valid for III–V nitride doped Mn or Cr, such AlMnN, AlCrN and GaMnN, respectively.

The lattice parameter of 'a' as function of concentration x for different compounds can be described approximately by

$$a = 4.47861 - 0.10321x - 0.0562x^2 \quad \text{For } Ga_{1-x}Cr_xN \tag{1}$$

$$a = 4.47451 - 0.0388x - 0.2425x^2 \quad \text{For } Ga_{1-x}Fe_xN \tag{2}$$

$$a = 4.48281 - 0.1601x - 0.0262x^2 \quad \text{For } Ga_{1-x}Mn_xN \tag{3}$$

$$a = 4.46752 + 0.1606x - 0.3324x^2 \quad \text{For } Ga_{1-x}V_xN \tag{4}$$

3.2 Electronic Properties

For magnetic systems, spin-polarisation calculations are performed using the concept of spin-up and spin-down electrons separately. We study the electronic structure of compounds and discuss the cause of the half-metallicity; the TM atom substituted for a cation site in GaN contributes three electrons to the anion dangling bonds. The d-electrons on

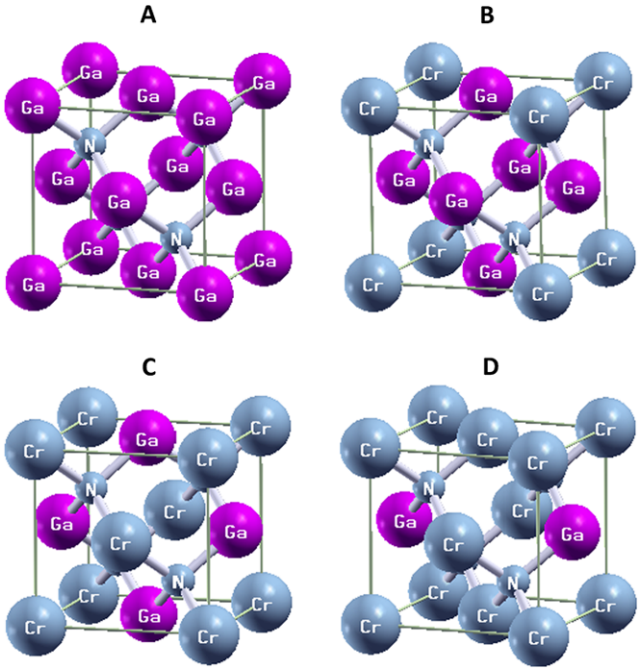

Fig. 1 Structures of Cr doped GaN: (**A**) GaN ($x = 0$), (**B**) $Ga_{0.75}Cr_{0.25}N$ (**C**) $Ga_{0.5}Cr_{0.5}N$ (**D**) $Ga_{0.25}Cr_{0.75}N$

Table 1 The calculated equilibrium constant a (Å), bulk modulos B (GPa), B'

Compound	x	a (Å)	B (GPa)	B'
$Ga_{1-x}Cr_xN$	0.00	4.4691	205.938	3.9715
	0.25	4.4661	216.2531	5.7232
	0.50	4.4196	189.2637	5.1872
	0.75	4.3439	245.1002	5.1862
$Ga_{1-x}Fe_xN$	0.00	4.4691	205.938	3.9715
	0.25	4.4638	199.4842	4.6864
	0.50	4.3850	205.4623	5.4488
	0.75	4.3076	268.3626	5.6413
$Ga_{1-x}Mn_xN$	0.00	4.4691	205.938	3.9715
	0.25	4.4669	206.966	5.3516
	0.50	4.4012	125.5645	1.5623
	0.75	4.3155	916.6179	38.2216
$Ga_{1-x}V_xN$	0.00	4.4691	205.938	3.9715
	0.25	4.4820	206.0678	5.0057
	0.50	4.4692	220.0170	5.3345
	0.75	4.3990	247.03565	4.5073

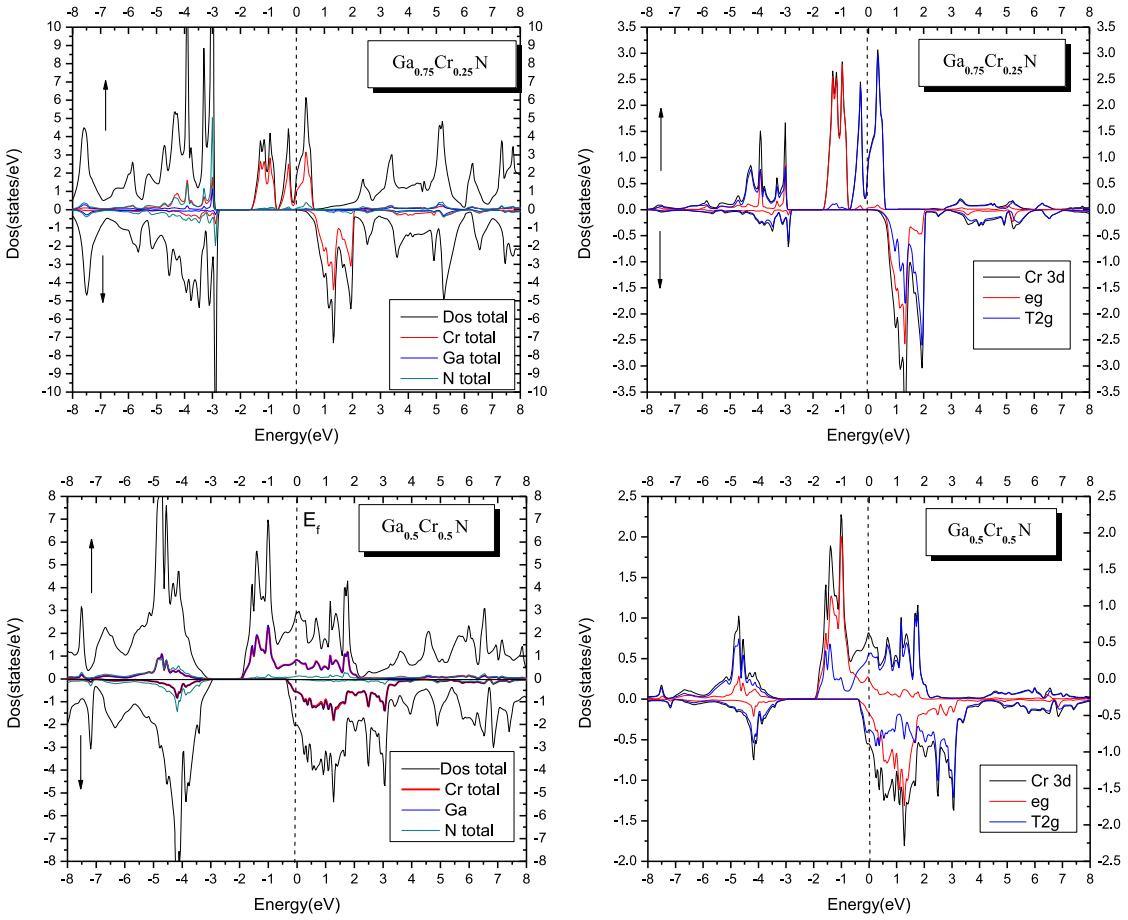

Fig. 2 Total and partial DOS for $Ga_{0.75}Cr_{0.25}N$ and $Ga_{0.50}Cr_{0.50}N$

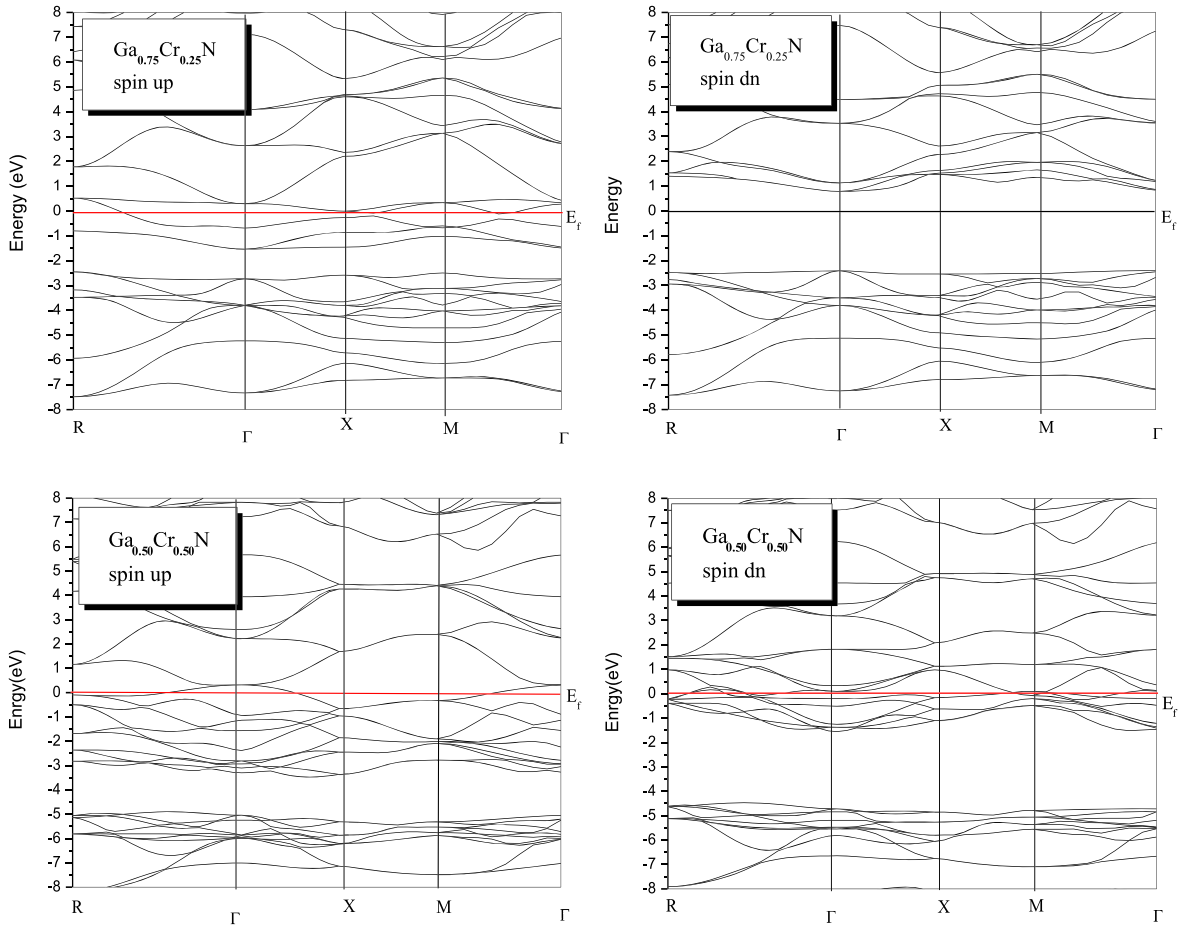

Fig. 3 Spin-polarised band structures for majority spin (*up*) and minority spin (*down*) for $Ga_{1-x}Cr_xN$

the doped TM atom site are responsible for its magnetic state. According to crystal field theory, the tetrahedral crystal field of surrounding anions splits the five-fold degenerate d states of a free TM ion into high lying t2g (d_{xy}, d_{yz} and d_{zx}) and low-lying eg (d_{z2} and d_{x2-y2})symmetry states [14], the energies of eg states are inferior than t2g states due to smaller Coulomb interactions, the magnetic state of a doped TM ion is the result of competition between crystal field splitting energy (the energy difference between t2g and eg states) and mean spin pairing energy (the energy required to pair up electrons in the state) [14], an important characteristic of a DMS is the existence of sp-d interactions between s; p band carriers of host semiconductor and d-electrons of doped TM ion [15]. The structures of the prototype of TM doped GaN with different concentrations are shown in Figs. 1, 4, 7 and Fig. 10.

Many of the most important character of the electronic structure of GaN doped with TM system can be seen from the band structures, the total DOS per unit supercell and the partial DOS of the TM impurity atom, different composition $x = 0.25$, 0.5 are presented in Figs. 2, 3 for $Ga_{1-x}Cr_xN$;

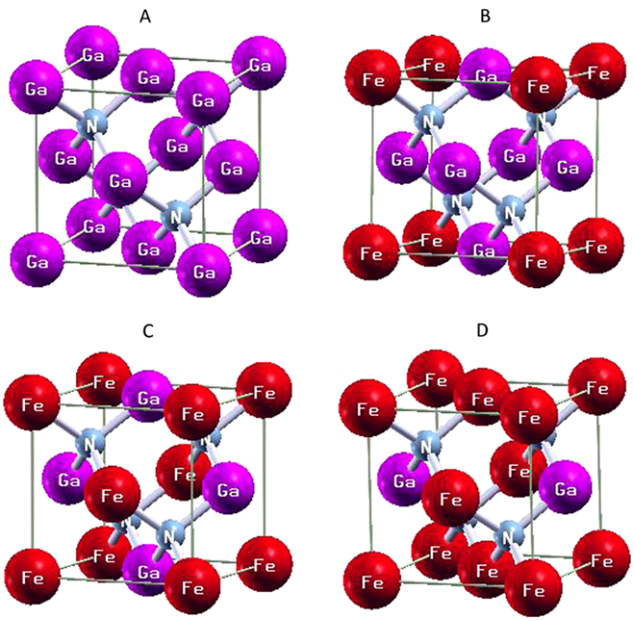

Fig. 4 Structures of Fe doped GaN: (**A**) GaN(x= 0), (**B**) $Ga_{0.75}Fe0_{.25}N$ (**C**) $Ga_{0.5}Fe_{0.5}N$ (**D**) $Ga_{0.25}Fe_{0.75}N$

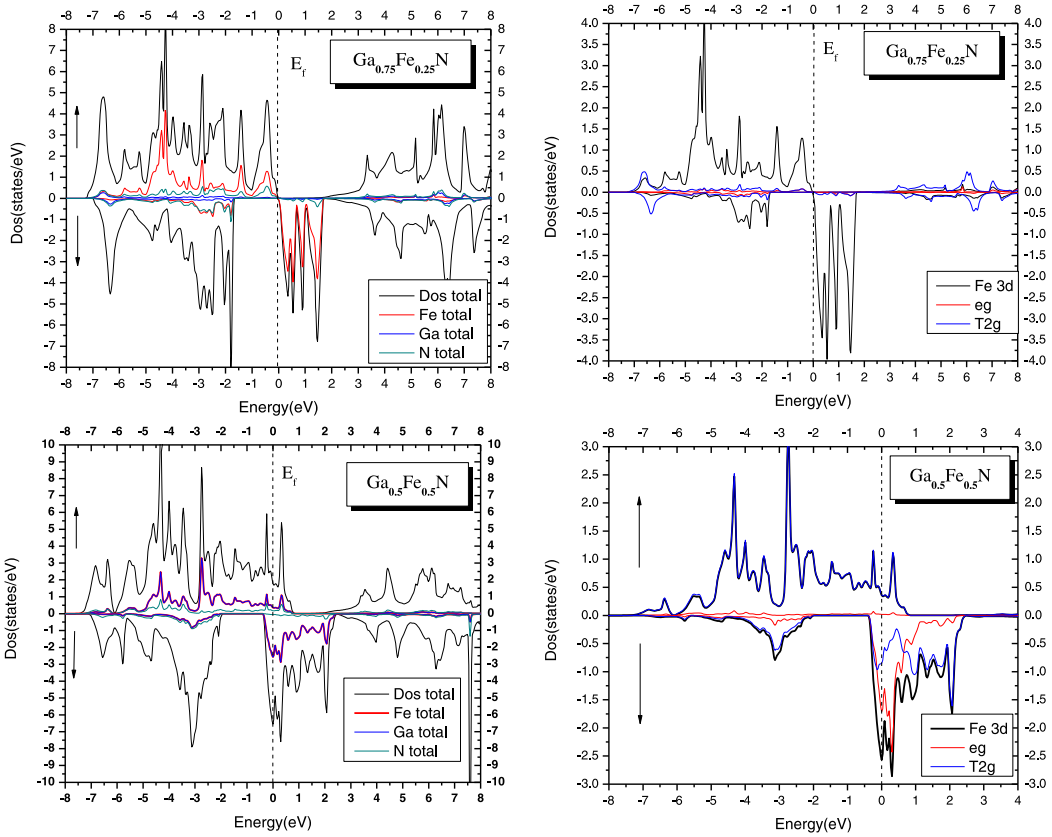

Fig. 5 Total and partial DOS for majority spin and minority spin for $Ga_{0.75}Fe_{0.25}N$ and $Ga_{0.50}Fe_{0.50}N$

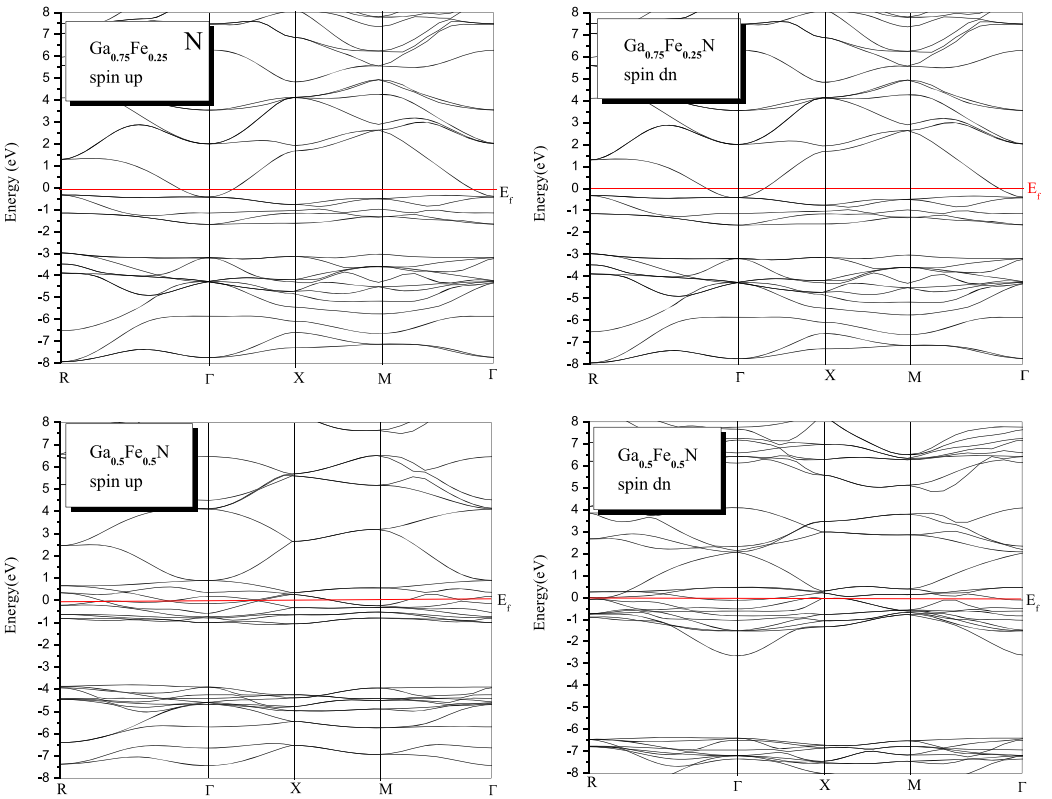

Fig. 6 Spin-polarised band structures for majority spin (*up*) and minority spin (*down*) for $Ga_{1-x}Fe_xN$

Table 2 Total and local magnetic moment in $Ga_{1-x}TM_xN$ (TM = Cr, Mn, Fe, V)

Compound	x	M^{tot} (μB/cell)	M^{TM}	m^{Ga}	m^{N}	$M^{interstitial}$
$Ga_{1-x}Cr_xN$	0	–	–	–	–	–
	0.25	2.9743	2.52775	0.01879	−0.05019	0.58811
		3.00 [14]	2.97 [14]		−0.070 [14]	
	0.50	5.99129	2.38568	0.03135	−0.03855	1.31120
	0.75	5.98881	1.76992	0.02706	−0.08593	
	1.00	–	–	–	–	–
$Ga_{1-x}Fe_xN$	0.25	0.00021	0.00013	0.00000	0.00000	0.00006
	0.50	7.94011	3.21024	0.03022	0.14203	0.88884
	0.75	0.45762	0.13986	0.00037	0.00257	0.04522
	1	–	–	–	–	–
$Ga_{1-x}Mn_xN$	0.25	4.00026	3.15397	0.02536	0.03112	0.64707
		3.98 [16]	3.313 [16]	0.028 [16]	0.002 [16]	0.517 [16]
	0.50	8.00029	3.44034	0.03501	0.02901	1.16421
		8.00 [16]	3.345 [16]	0.057 [16]	0.008 [16]	1.16 [16]
	0.75	12.00037	3.48362	0.05061	−0.03895	1.65102
	1	–	–	–	–	–
$Ga_{1-x}V_xN$	0.25	1.96097	1.54329	0.01585	−0.02497	0.47110
		2.00 [14]	2.039 [14]		−0.046 [14]	
	0.50	3.98543	1.57450	0.02793	−0.06468	1.03934
	0.75	0.22593	0.05894	0.00242	−0.00070	0.04812
	1	–	–	–	–	–

Figs. 5, 6 for $Ga_{1-x}Fe_xN$; Figs. 8, 9 for $Ga_{1-x}Mn_xN$ and finally Figs. 11, 12 for $Ga_{1-x}V_xN$.

First of all we observe for Cr, Mn and V doped GaN at $x = 0.25$ a half-metallic behaviour in the sense that the Fermi level state density is finite for the majority spin and zero for the minority spin, the majority spin DOS is metallic but the minority spin density of states is semiconducting. For Fe we can see the absence of half-metallic character for all concentrations. For $x = 0.50$ the ternary compounds lose the half-metallic character. As exposed by the density of states, for all the $Ga_{1-x}TM_xN$ compounds the valence band is dominated by the TM (TM = Cr, Mn, Fe, V) d and N p orbital. The valence band between −7 and −3 eV comes mainly from the N p-states for $Ga_{0.75}Cr_{0.25}N$.

3.3 Magnetic Properties

In Table 2 we show a result of the calculations made with the theoretical method we adopted. The total magnetic moment of the unit cell, for the alloys $Ga_{1-x}TM_xN$, (TM = Cr, Mn, Fe, V) for $x = 0.25$, $x = 0.50$, $x = 0.75$ is decomposed in the contributions of the atomic spheres of Ga, N, TM and of the interstitial region for each angular momentum. The total magnetisation of the cell is 3 μB for $Ga_{0.75}Cr_{0.25}N$, the magnetic moments inside the atomic spheres are ∼2.52 μB for Cr, ∼0.01 for Ga and ∼0.588 in the interstitial region. For $Ga_{0.75}Mn_{0.25}N$, $Ga_{0.5}Mn_{0.5}N$ and $Ga_{0.25}Mn_{0.75}N$ the total magnetic moment is 4 μB, 8 μB and 12 μB, respectively. Considering that the total magnetic

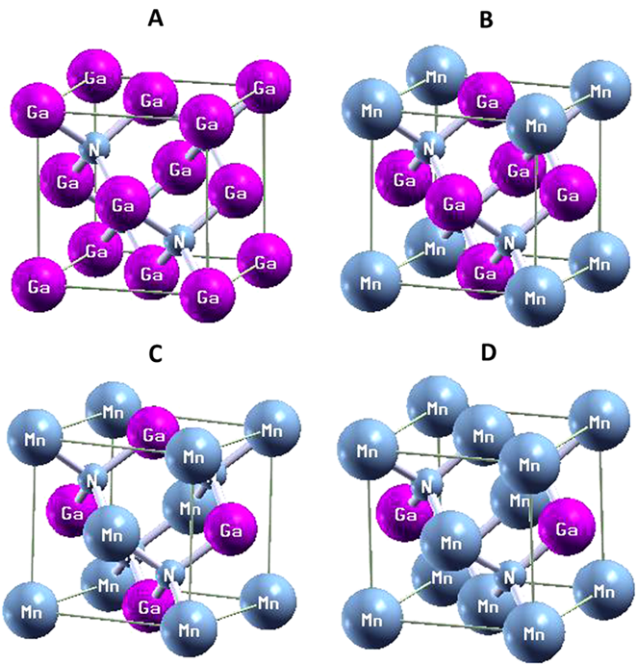

Fig. 7 Structures of Mn doped GaN: (**A**) GaN ($x = 0$), (**B**) $Ga_{0.75}Mn0_{.25}N$ (**C**) $Ga_{0.5}Mn_{0.5}N$ (**D**) $Ga_{0.25}Mn_{0.75}N$

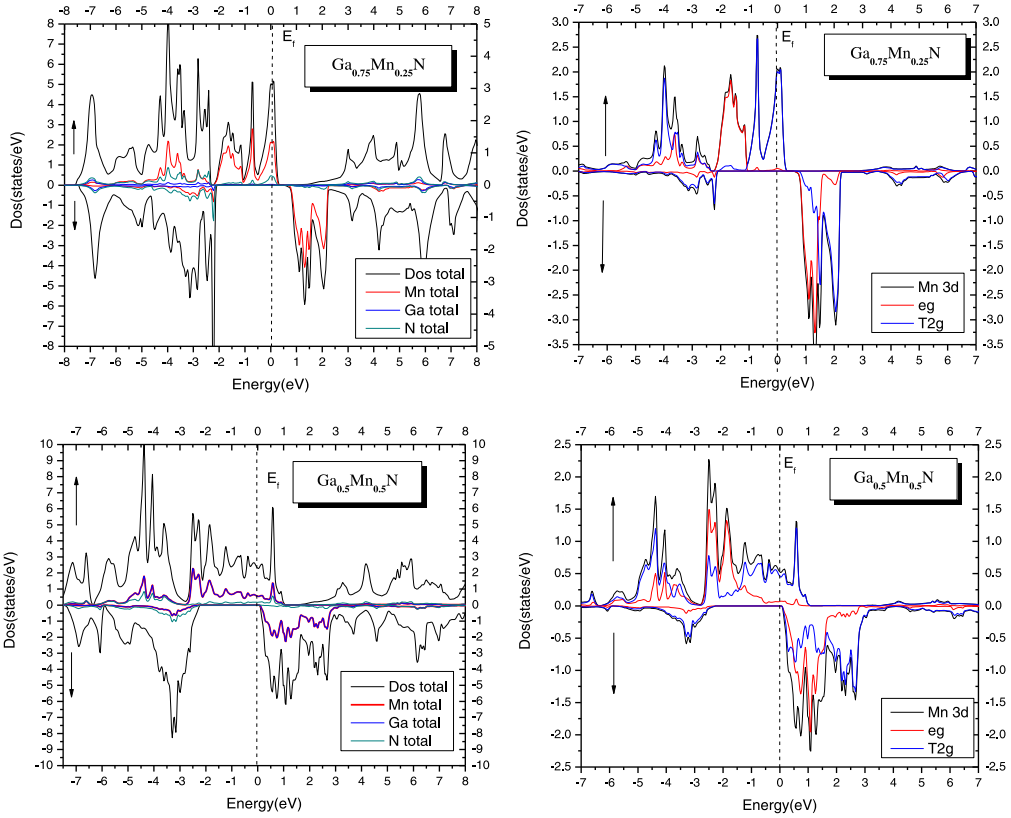

Fig. 8 Total and partial DOS for majority spin and minority spin for $Ga_{0.75}Mn_{0.25}N$ and $Ga_{0.50}Mn_{0.50}N$

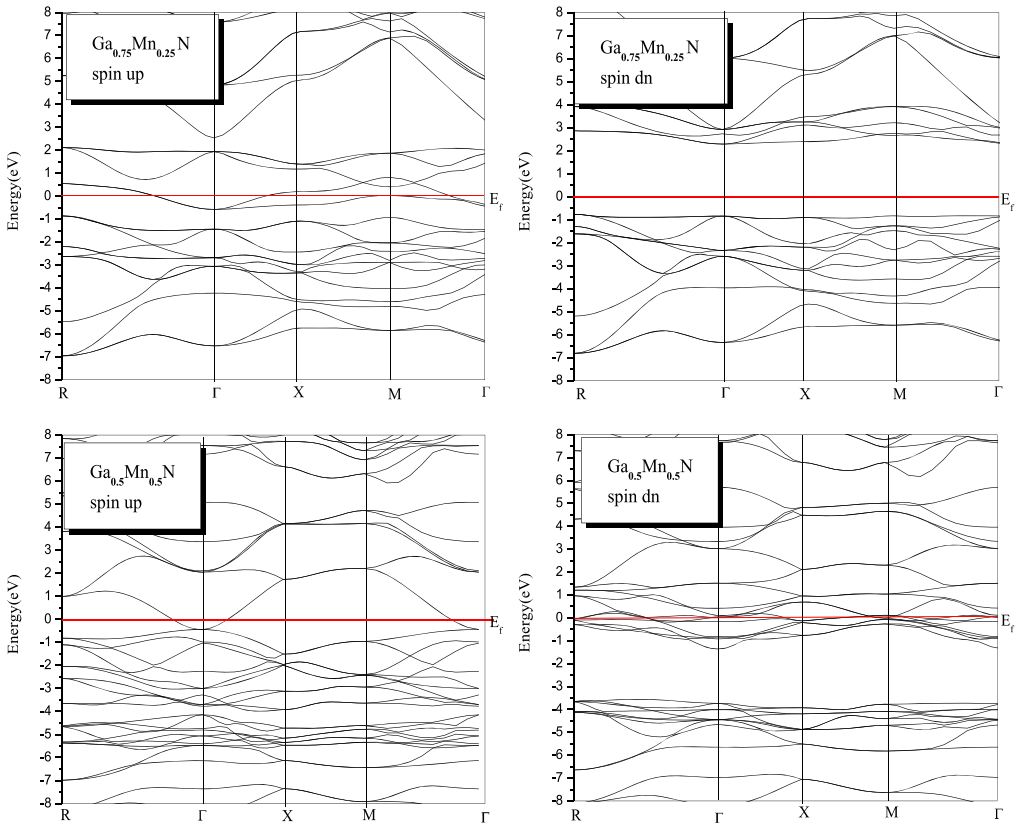

Fig. 9 Spin-polarised band structures for majority spin (*up*) and minority spin (*down*) for $Ga_{1-x}Mn_xN$

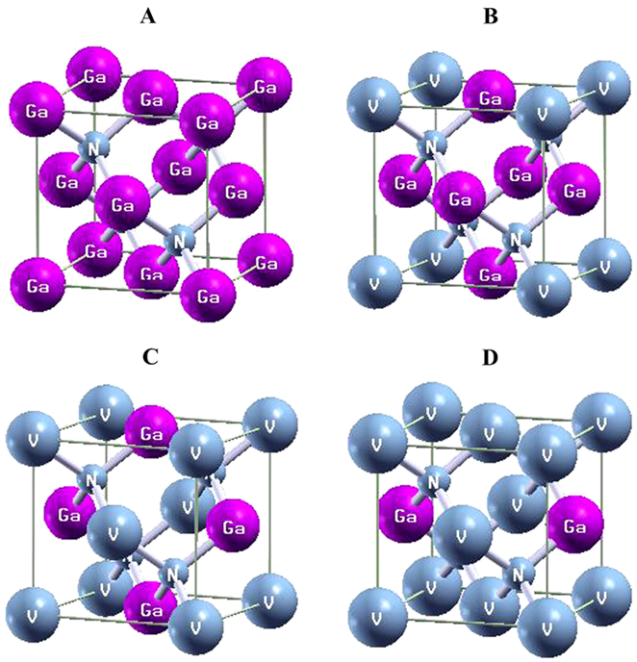

Fig. 10 Structures of V doped GaN: (**A**) GaN ($x = 0$), (**B**) $Ga_{0.75}V_{0.25}N$ (**C**) $Ga_{0.5}V_{0.5}N$ (**D**) $Ga_{0.25}V_{0.75}N$

moment is typically of the character of half-metallic compounds, it can be seen from Table 2 that the total magnetic moments of all compounds are mainly from the TM atom, and the contributions from Ga, N and the interstitial are very small.

The hybridisation between TM ion and N ions plays an important role in the formation of induced magnetic moments. The V and Cr ions induce antiferromagnetic interactions in the neighbouring N atom of GaN, while Fe ion induce ferromagnetic interactions in surrounding Ga and N atoms of GaN host semiconductor, the substitutional doping of a TM ion at a Ga site change the number of spin-up and/or spin-down states in the valence band of GaN. The V, Cr, Mn and Fe have two, three, four and five extra electrons, respectively. For V, Cr and Mn the spin-up valence appear unoccupied states, these impurity hole states are of spin-up type. Due to hybridisation between N and TM ions these hole states of TM ion become partly occupied and consequently spin-down states of N become more occupied than spin-up states. This gives rise to induced magnetic moment in N atoms antiparallel to that of TM (V, Cr) ions. In case of

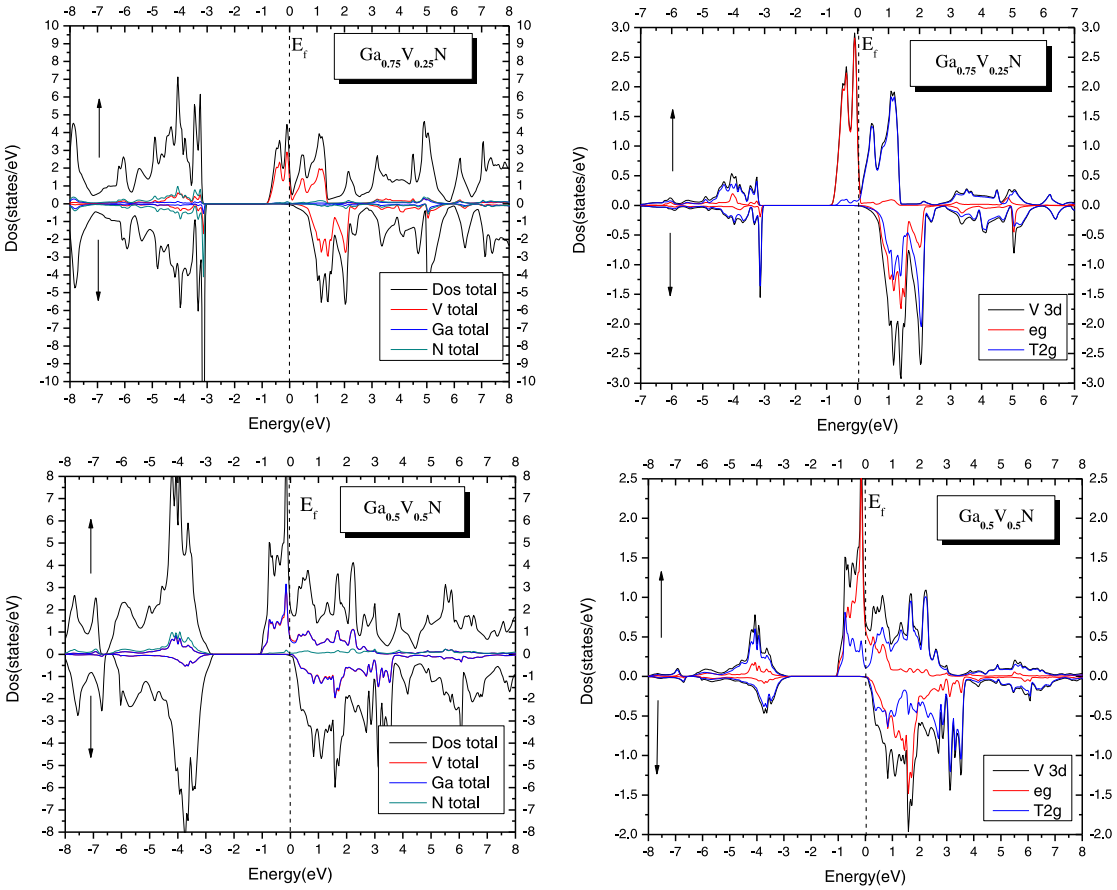

Fig. 11 Total and partial DOS for majority spin and minority spin for $Ga_{0.75}V_{0.25}N$ and $Ga_{0.50}V_{0.50}N$

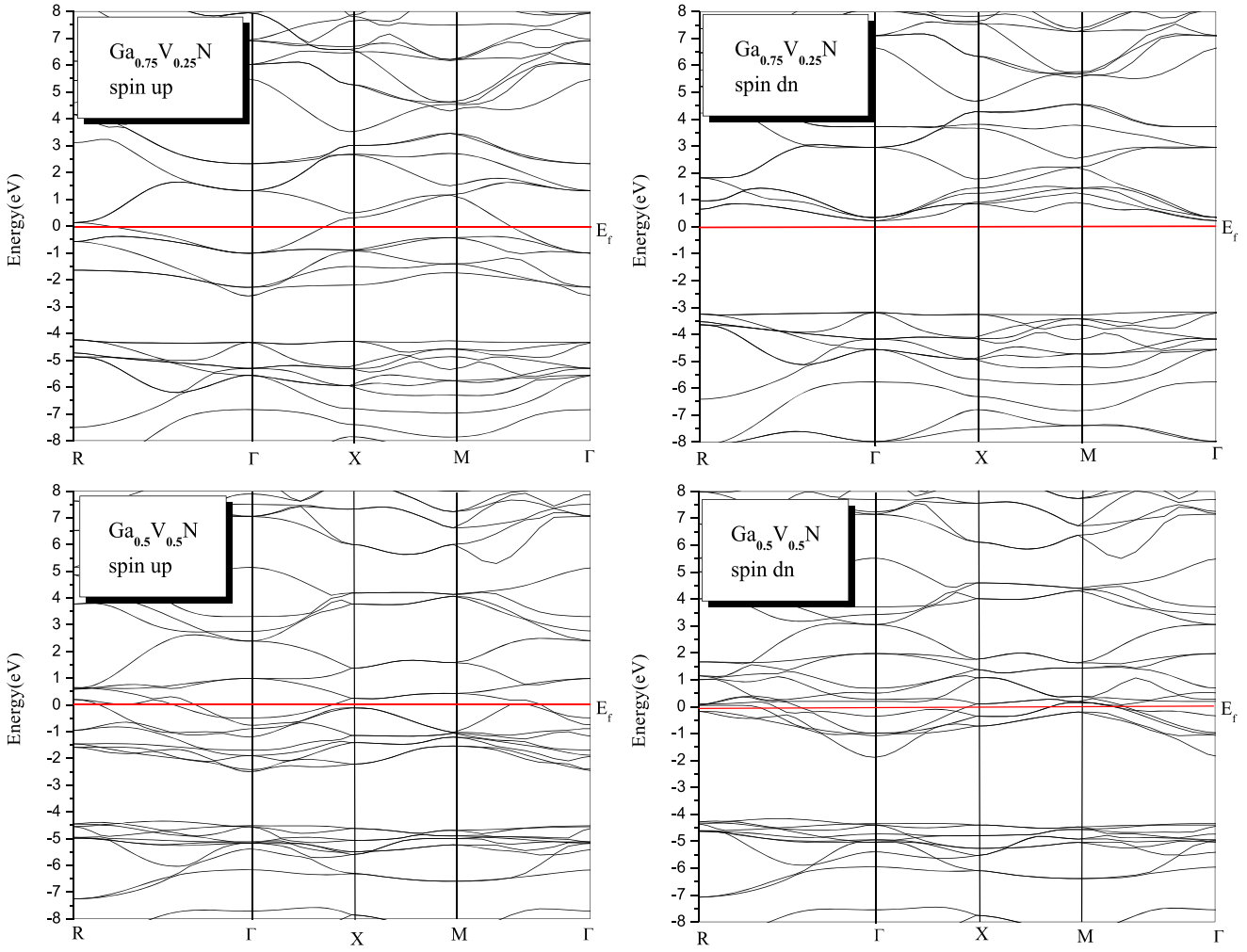

Fig. 12 Spin-polarised band structures for majority spin (*up*) and minority spin (*down*) for $Ga_{1-x}V_xN$

Fe all the spin-up states are occupied, but spin-down states are in either case empty.

4 Conclusion

In the present work, we have performed the first principles calculations of structural, electronic and magnetic properties of cubic $Ga_{1-x}TM_xN$ (TM = Cr, Mn, Fe, V) with 25 %, 50 % of TM, and we found a large deviation from Vegard's law for the variation in the lattice parameter.

The calculated densities of states (partial and total) presented in this study identify that $Ga_{0.75}TM_{0.25}N$ (TM = Cr, Mn, V) display a half-metallic characteristic for all TM atom compositions; this characteristic disappears for $x = 0.5$, for Fe the half-metallic character is absent for all concentrations.

The total magnetic moments in all alloys come mainly from the TM atom, and the contributions from Ga and N, are smallest.

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