Structural phase transitions of Ga(Mn)N under high pressure

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Abstract. Gallium nitride doped with a small concentration of manganese ($Ga_{1-x}Mn_xN$) is one of diluted magnetic semiconductors which can be used for spintronic applications. In this work, $Ga_{31}Mn_1N_{32}$ in the zinc blende (ZB) and rock salt (RS) structures were investigated. We employed the density functional theory (DFT) within the generalized gradient approximation (GGA) to study structural properties, the density of states and the magnetization. The structural phase transitions under pressure up to 60 GPa were also studied. We found that $Ga_{31}Mn_1N_{32}$ in the ZB phase is stable at ambient pressure, and change to the RS phase at about 42 GPa. By using GGA+U, the absolute magnetization is 4.68 μ_B per cell at 0 GPa. We found also that the absolute magnetization is reduced under pressure.

1. Introduction

In the past decades, the binary compound semiconductors, both II-V and III-VI types, are extensively studied because of a variety of applications, such as light-emitting diodes (LEDs), laser diodes, photo detectors and photovoltaic cells. Gallium nitride (GaN) is one of the most promising materials for short wavelength optoelectronic devices because of its unique optical and electronic properties. GaN has wide and direct band gaps (3.18 and 3.39 eV for zinc blende (ZB) and wurtzite (WZ) crystal structures, respectively) [1], a high melting point (2770 K for the ZB structure) [2], a high thermal conductivity (1.3 W/(cm• K) at 300 K) and a large bulk modulus (204 and 210 GPa for ZB and WZ structures, respectively) [3, 4]. Also, it can be doped with a small concentration of magnetic impurities, i.e. atoms of transition metals such as Mn, Co and Cr. These materials are called the diluted magnetic semiconductors (DMSs). GaN doped with Mn ($Ga_{1-x}Mn_xN$) is regarded as a prospect candidate for the spintronic applications, such as super smart diodes and spin value transistors. Moreover, $Ga_{1-x}Mn_xN$ was found to have high curie temperature (T_c), i.e. upto 940 K [5, 6]. Thus, the theoretical calculations of the structural modifications and the various concentrations of Mn in GaN lead to understanding and prediction of its electronic and magnetic properties.

Table 1. Lattice parameters of GaN compared with data from previous works.

Lattice parameter of GaN (Å)		Our calculations			Previous works [16]		
		Quantum-ESPRESSO	CASTEP		Theoretical data		Experiments
		GGA	GGA	LDA	GGA	LDA	
ZB	a	4.548	4.461	4.557	4.530, 4.55, 4.59	4.446, 4.461, 4.464, 4.537	4.5
WZ	a, b	3.218	3.224	3.155	3.205, 3.224, 3.245	3.157, 3.177, 3.193	3.18, 3.192, 3.186
	c	5.242	5.253	5.145	5.220, 5.25, 5.296	5.0, 5.14, 5.184, 5.228	5.166, 5.178, 5.185
RS	a	4.267	4.277	4.188	4.252, 4.263, 4.271	4.183, 4.185, 4.19, 4.24	-

2. Computational method

In this work, *ab-initio* calculations were performed by using the density functional theory (DFT) [7, 8] and the self-consistent field method, as implemented in the Quantum-ESPRESSO code [9]. We used the Perdew-Burke-Ernzerhof (PBE) functional for the generalized gradient approximation (GGA) [10, 11], and also used the CASTEP code within the GGA and LDA for comparison [12]. The kinetic energy cutoff and k-point grid of the wave functions in the plane wave basis set were chosen at 70 Ry and 8×8×8 grid for geometry optimization. At ambient pressure, we investigated pure GaN with zinc blende (ZB), wurtzite (WZ), and rock salt (RS) structures. For GaN doped with a small concentration of manganese atoms (Mn), it has been found experimentally that Mn occupies the Ga site [13]. Therefore, we investigated a 2×2×2 supercell based on the conventional cell of GaN both in the ZB and RS unit cells (64 atoms), the Ga atom at center of supercell was replaced by a Mn atom (yellow ball in Figure 1). Thus the concentration of Mn is 3.125 % ($Ga_{31}Mn_1N_{32}$). For calculating the magnetic properties, the spin-orbit coupling and Hubbard U method (DFT+U) were included because of the highly correlated 3d orbitals of Mn [14]. The U parameter of Mn in this work was chosen to be 3.9 eV [15].

3. Results and discussion

The calculated lattice parameters of GaN are presented in Table 1. Our calculations are generally in good agreement with other theoretical and experimental data [16]. At ambient condition, we determined the bond lengths of the Ga atom with its nearest neighbor atoms.

Figure 1. $Ga_{31}Mn_1N_{32}$ with (a) ZB, and (b) RS structures.

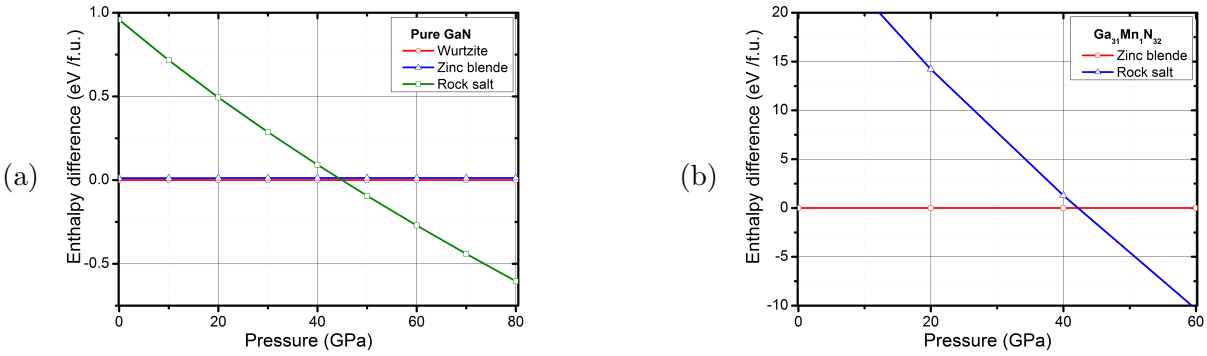

Figure 2. Enthalpy difference for (a) GaN and (b) $Ga_{31}Mn_1N_{32}$ under high pressure.

The average value of *Ga–N* bond lengths are 1.969 and 1.971 Å for GaN and $Ga_{31}Mn_1N_{32}$, respectively. The extension of *Ga–N* should be compensated for the shortened *Mn–N* bond lengths of 1.907 Å (shortened by 3.2 %).

The calculations of the enthalpy as a function of the external pressure in the range of 0 to 80 GPa (to 60 GPa for GaMnN) were performed at 0K, as shown in Figure 2. The enthalpy difference compared with the WZ phase for GaN (shown in Figure 2 (a)) shows that both the ZB and WZ phases have same enthalpy, i.e. the difference is less than 1.3×10^{-2} eV/f.u., and lower than that of the RS phase at low pressure. Thus both ZB and WZ phases are stable at low pressure. The phase transition from both the ZB and WZ to the RS phase are at 44.2 and 44.9 GPa, respectively, which is comparable with other theoretical and experimental data [16], as presented in Table 2. The enthalpy difference for $Ga_{31}Mn_1N_{32}$ (See in Figure 2 (b)) shows that the ZB phase is stable than the RS phase at low pressure, and changes to the RS phase at 42.2 GPa, as presented in Table 2. Our results show that Mn doped in GaN has significant influence to the phase transition.

The calculated partial density of states (PDOS) of $Ga_{31}Mn_1N_{32}$ in the ZB phase using DFT $+U$ method are presented in Figure 3. We choose the PDOS of 3*d*-Mn, 4*p*-Mn, and 2*p*-N (the red, green, and purple lines, respectively, in Figure 3). The 2*p*-N PDOS is taken from the nearest neighbors of the Mn atom only, as the Mn atom have the strongest influence on the electron spins of its nearest neighbor atoms. We found that these PDOS of 3*d*-Mn, 4*p*-Mn, and 2*p*-N dominatedly occupy the states near the fermi level (set to 0 eV), which also favor spin polarized states. We calculated the magnetizations for $Ga_{31}Mn_1N_{32}$. We found that the absolute magnetization per cell at ambient condition is 4.68 μ_B per cell. Furthermore, it is reduced under pressure to be 4.50, 4.40, and 4.32 μ_B (for pressure at 20, 40, and 60 GPa, respectively). By closer examining the PDOS, we found that the influence of the Mn atom on the electron spins of its nearest neighbor atoms becomes gradually weakened under pressure.

Table 2. Phase transition of GaN and $Ga_{31}Mn_1N_{32}$ compared with data from previous works.

Structural phase transition (GPa)		**Our calculations (Quantum-ESPRESSO)**	**Previous works [16]**		
			Theoretical data		**Experiments**
		GGA	**GGA**	**LDA**	
GaN	ZB → RS	44.2	40.80, 42.44	36.84, 38.15, 38.21, 42.6	–
	WZ → RS	44.9	45, 45.8	41.7, 42, 42.9, 42.9	37, 42, 47, 52.2
$Ga_{31}Mn_1N_{32}$	ZB → RS	42.2	–	–	–

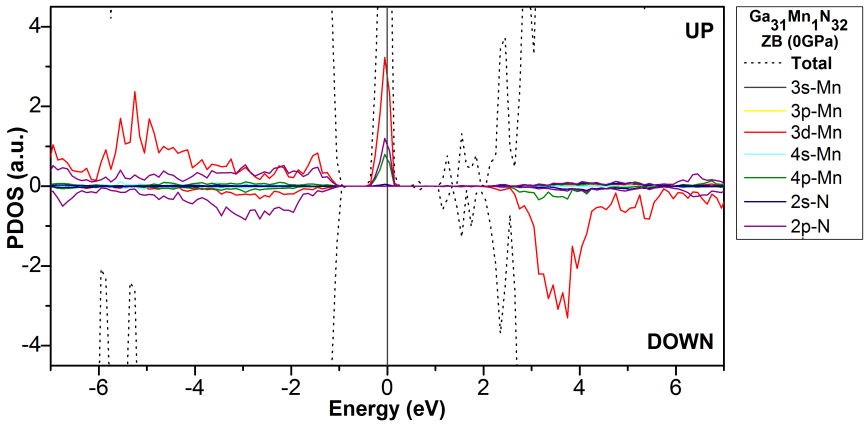

Figure 3. Partial density of states of $Ga_{31}Mn_1N_{32}$ in the ZB phase at pressure is 0 GPa

4. Conclusion

We have applied the DFT as implemented in the Quantum-ESPRESSO code within the GGA functional for investigating the properties of GaN and $Ga_{31}Mn_1N_{32}$. The phase transition of GaN and $Ga_{31}Mn_1N_{32}$ from the ZB to RS phase is at 44.2 and 42.2 GPa, respectively. The absolute magnetization is 4.68 μ_B per cell at ambient conditions, and decreases considerably under high pressure.

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References

[1] Maruska H P and Tietjen J 1969 *Applied Physics Letters* **15** 327–329
[2] Harafuji K, Tsuchiya T and Kawamura K 2004 *Journal of applied physics* **96** 2501–2512
[3] Wright A 1997 *Journal of Applied Physics* **82** 2833–2839
[4] Mion C 2005 *Investigation of the thermal properties of gallium nitride using the three omega technique* Ph.D. thesis Electrical Engineering, A dissertation submitted to the Graduate Faculty of North Carolina State University
[5] Reed M, El-Masry N, Stadelmaier H, Ritums M, Reed M, Parker C, Roberts J and Bedair S 2001 *Applied Physics Letters* **79** 3473–3475
[6] Saito H, Zayets V, Yamagata S and Ando K 2003 *Physical review letters* **90** 207202
[7] Hohenberg P and Kohn W 1964 *Physical review* **136** B864
[8] Kohn W and Sham L J 1965 *Physical review* **140** A1133
[9] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti G L, Cococcioni M, Dabo I *et al.* 2009 *Journal of physics: Condensed matter* **21** 395502
[10] Perdew J P, Burke K and Ernzerhof M 1996 *Physical review letters* **77** 3865
[11] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Physical Review B* **46** 6671
[12] Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M I, Refson K and Payne M C 2005 *Zeitschrift für Kristallographie-Crystalline Materials* **220** 567–570
[13] Sato M, Tanida H, Kato K, Sasaki T, Yamamoto Y, Sonoda S, Shimizu S and Hori H 2002 *Japanese journal of applied physics* **41** 4513
[14] Anisimov V I, Aryasetiawan F and Lichtenstein A 1997 *Journal of Physics: Condensed Matter* **9** 767
[15] Mueller T, Hautier G, Jain A and Ceder G 2011 *Chemistry of materials* **23** 3854–3862
[16] Saoud F S, Plenet J, Louail L and Maouche D 2011 *Computational and Theoretical Chemistry* **964** 65–71