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Density Functional Theory Studies of the Electronic and Optical Properties of Zinc Blende InN under High Pressure*

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Abstract: First-principles density functional studies of the properties of zinc blende InN are presented. We have employed density functional theory, as implemented in the CASTEP code, to investigate the electronic, elastic and optical properties of the material zinc blende InN under hydrostatic pressure range up to 70 GPa. The optimized geometrical lattice constant of InN in the ground state obtained by using generalized gradient approximation is in good agreement with existing results and the lattice constants with pressure increasing. The calculated partial densities of states (PDOS) of the material have two regions in the valence band of InN. It is shown that the PDOS is quite low in the vicinity of the Fermi level, implying that it tends to form stable structure but has a poor conductivity. The elastic tensor components have linear scaling with pressure, C_{11}, C_{12} and B have a positive scaling with pressure. Whereas C_{44} and C_s have a negative scaling. The absorption spectra move towards the shorter wavelength direction. The shape of the spectra has almost no change when pressure increases. The results presented in this work is helpful for re-evaluating much of the pressure dependence of the properties for the material InN.

Key words: zinc blende InN; electronic and optical properties; density functional theory; high pressure

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1 Introduction

Indium nitride(InN) is among the Ⅲ-Ⅴ nitride semiconductors. In the last two decades, InN and its cousins, such as GaN and AlN, have attracted increasing attention due to both their technological applications of optoelectronic devices in the blue and ultraviolet spectral region as swell as for high

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power electronics[1-2]. In contrast to GaN or Ga-rich InGaN, which are regarded as efficient light emitters even at relatively high defect concentrations, InN has been the least studied among the group Ⅲ nitrides. Since InN usually has a hexagonal wurtzite phase, most of the research has been concentrated on the InN wurtzite crystal lattice[3-4]. Due to the progress made in the material InN cubic phase doping and growing, there are some studies of the properties of the material InN in the zinc blende phase[5-7]. Experimentally, optical absorption studies[8] on sputtered InN films suggested a fundamental band gap of about 1.9 eV. However, some people studied[9-10] the optical and electronic structure of molecular-beam epitaxy (MBE) grown InN and In-rich group Ⅲ-nitride alloy films, the band gap of wurtzite InIN was determined to be 0.7 eV by optical absorption, photoluminescence, and photo-modulated reflectance. The narrow gap suggested[9] weaker pressure dependencies than those of GaN and AlN.

It is known that knowledge of the electronic structures of the material is very important for improving quality of light devices. Study of the pressure effect of semiconductor could provide valuable insight about these materials. Theoretically, by employing the Ceperley[11] form exchange-correlation functional, Saib[12] studied the pressure induced phase transformation of the material by *ab initio* calculations, and their results were roughly in good agreement with the available experimental data. Kanoun[13] predicted the pressure dependence of elastic modulus for zinc blende InN using full-potential augmented-plane wave plus local orbitals (FP-APW+Lo) calculations with density functional theory in local density approximation, and they found a linear dependence of bulk modulus and elastic constants with the pressure applied. Bouarissa studied the electronic and lattice properties of the zinc-blende InN under high pressure[7] by using empirical pseudopotential method, and the dependencies of electronic structure and lattice properties of InN with zinc-blende structure on hydrostatic pressure were presented based on band structures computed using the empirical pseudopotential method. Still others[14] studied the energy band structures of InN for few volumes corresponding to hydrostatic up to 10 GPa. The InN energy gap increases sublinearly with hydrostatic pressure with the pressure coefficient which was in quite good agreement with experimental data[15].

Though there has been growing experimental and theoretical interests for pressure behaviour of the electronic and structural properties for the group Ⅲ nitrides. However, uncertainties remain concerning the basic aspects of the material InN, such as the band gap anomaly[4]. Furthermore, there has much less investigations for zinc-blende InN, and in some case, the theoretical work was only studied empirically[7]. Up to now, no comprehensive studies are available regarding the electronic, elastic, and optical properties of the zinc-blende InN under high pressure. Therefore, it has become necessary to re-evaluate much of the pressure dependence of the properties for the material InN.

In order to provide some detailed information on the physical properties of zinc-blende InN under high pressure, we have computed the electronic, elastic and lattice properties of zinc-blende InN using the first-principles density functional theory (DFT) method. We will focus on the properties dependence on hydrostatic pressure. In this work we present a first-principles investigation of the dynamical properties of InN under high pressure. Firstly, we will study on the geometrical and the structural properties of InN. Then a detailed analysis is performed to investigate the pressure induced effects on the electronic, elastic and optical for zinc-blende InN. The paper is organized as follows: Sec. 2 presents the calculation model and computational details, and then in Sec. 3 we present the results and discussion. A short summary concludes the paper in Sec. 4.

2 Computational Details

The calculations were performed with the plane wave ultrasoft pseudopotential method implemen-

ted in CASTEP[16-18] quantum mechanics software package. Such calculations have been successful in giving accurate and reliable structural and electronic information for a variety of systems[19-23]. To minimize the number of plane waves, we apply ultrasoft pseudopotential[24] to describe the ion-cor interaction with the valence electrons.

The cut-off energy was selected as 400 eV, which ensures convergence of the total energy difference of the system to 1.0 meV/cell. The generalized gradient approximation (GGA), using Perdew[25] exchange and correlation functional, was employed in the present calculations. In the optimization of geometry, the Hellmann-Feynman[26] force on each atom was calculated. The atoms move under these forces until no force exceeds some threshold value. This allows us to find the structure that is the nearest local minimum to the starting configuration. The Pulay mixing scheme was used to achieve self-consistency between the input and output potentials. For all these simulations, point group symmetry was not enforced since small symmetry breaking may occur. The Monkhorst-Pack k-point sampling[27] of $6\times6\times6$ mesh, was utilized to perform the integrations in k-space over the Brillouin zone, with the grids for each cell chosen to be dense enough to converge the total energy to 1.0 meV/atom. Zinc blende InN belongs to cubic crystal system and the space group is $F\text{-}43M(216)$. There are 4 In and 4 N atoms in the conventional cell. In the calculations, the involved valence electron configurations are N $2s^2 2p^3$, In $4d^{10} 5s^2 5p^1$.

3 Results and Discussion

3.1 The Geometrical Properties of InN

We first optimized InN geometrical structures of the ground state using the Hellman-Feynman force[26]. After geometry optimization by using GGA, the lattice parameter a of the InN crystal is 0.504 nm, which is slightly larger than the experimental value 0.498 nm[28]. In the process of geometry optimization, we found that when the pressure is up to 80 GPa, there was a bond breaking in the crystal structure. So, we study the properties of InN under the pressures 0, 10, 20, 30, 40, 50, 60, 70 GPa. The relationship between the lattice parameter and pressure was shown in Fig. 1, it can be seen that the parameter becomes smaller with the increase of pressure. This is due to the pressure makes the crystal more compactable, so that the lattice parameter becomes smaller. The inset in Fig. 1 shows the relationship between the total energy and the pressure. It can be found that when pressure increases from 0 to 10 GPa, the total energy has a slow increase. But when the material is under the pressure range from 20 to 70 GPa, the total energy almost has a linear increase with pressure. This is due to the fact that with the pressure increases, the potential energy becomes big, thus makes the energy large.

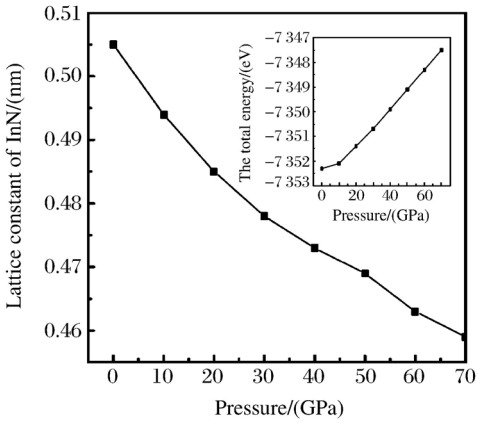


Fig. 1 Calculated pressure dependence of the lattice parameter
(The inset in the figure shows the relationship between the total energy and pressure)

3.2 The Electronic Properties under Zero Pressures

The calculated partial densities of states (PDOS) and band structure of zinc blende InN under zero pressures are presented in the Figs. 2 and 3. It can be found from the PDOS in Fig. 2 that there two

regions in the valence ban of InN, that is the lower band in the energy region −14.53 to −10.74 eV and the upper band in the region −5.69-0 eV. The upper band mainly consists of N 2*p* electrons, and a few In 5*s* electrons. The In 4*d* electrons contribution to the majority of the lower band, and some N 2*s* electrons also make a little contribution to the lower band. There is a strong In 4*d* localized state at −13.26 eV, much stronger in the intensity than that of the N 2*s* electrons. The conduction band is mainly from In 5*s*5*p*, N 2*p* electrons, the density of states in this quite scattered. It can also be seen from the band structure in Fig. 3, at point *G*, there is a direct band gap of 0.34 eV.

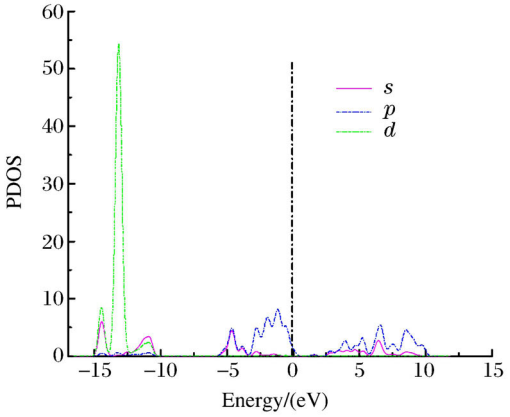


Fig. 2 (Color online) Partial density of states of InN under 0 Pa

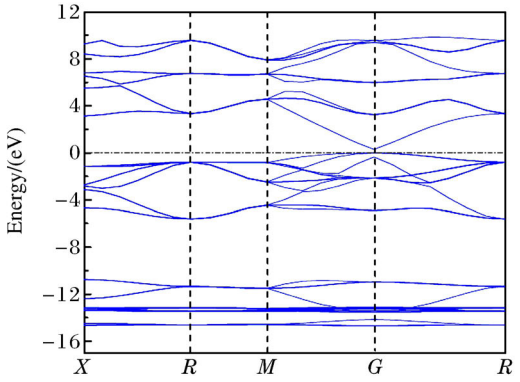


Fig. 3 (Color online) Band structure of zinc blende InN under 0 Pa. The *k* point coordinates are: *X*(0.5,0,0), *R*(0.5,0.5,0.5), *M*(0.5,0.5,0), *G*(0,0,0)

3.2.1 Densities of States of Atoms In and N

In order to observe the evolution of the electronic structure of atoms In, N under pressure in the crystal InN, Fig. 4 and 5 show the partial densities of states (PDOS) distribution under the pressures 0, 10, 20, 30, 40, 50, 60, 70 GPa for the atoms In, N in the InN crystal. From the figures, it can be found that, with the increase of pressure, the electrons in the valence band moved slightly towards lower energy direction, whereas the electrons in the conduction band go towards the higher energy direction, this will result in the larger band gap. Since In is a transitional element, the *d* electrons dominate the physical properties, so we only discuss the densities of states of *d* electrons in Fig. 4. There are two peaks when the pressure is relatively low, one peak is dominantly larger and sharper than the other, this peak has strong locality. When the pressure is up to 60 GPa, the peak becomes slightly flat, and has some splitting at 70 GPa. With the increase of pressure, the peak value of the PDOS is becoming lower, and the *d* electrons DOS moves towards lower energy direction and distributes wider. It can be found that at zero pressures, the DOS is in the region from −10.28 to −14.96 eV with energy width of 2.41 eV. When the pressure is at 70 GPa, the DOS distribution region is in the −10.42 to −16.87 eV, that is with width of 5.04 eV, this width is more than double that of at zero pressure, and also has very strong nonlocality. In Fig. 5, the N 2*s* electrons are mainly in the valence region. With increase of pressure, the DOS moves towards lower energy direction, and distributes wider and the peak value is becomes larger. For the N 2*p* electrons, with the increase of pressure, the peak values of DOS in both valence and conduction band become smaller. Especially those electrons which in the conduction band, the peak value becomes obviously smaller and has strong nonlocality. The *p* electrons in the conduction band move toward higher energy direction, and result in a larger band gap. We found that at zero and high pressure, the DOS in the vicinity of the Fermi level is relatively low, indicating that the electrons in the valence band have a smaller transition chance to the conduction band. This implies that it tends

to form stable structure but has a poor conductivity. The N 2*s* and In 3*d* electrons have overlaps and hybridization in the region from −10 to −15 eV, indicating that hybrid phenomena appear at low pressure, and the hybrid becomes not very obvious when pressure increases.

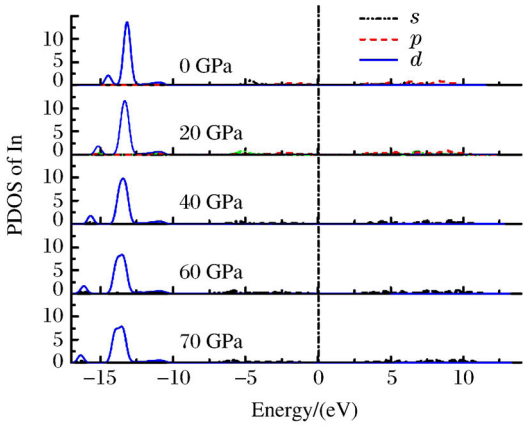


Fig. 4　(Color online) Partial densities of states of atom In in the material InN under pressure

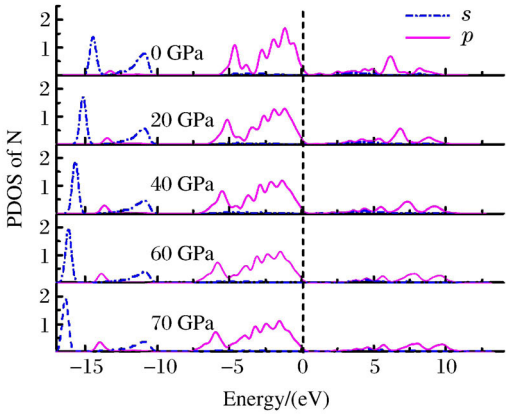


Fig. 5　(Color online) Partial densities of states of atom N in zinc blende InN under pressure

3.3　Elastic Constants of InN

For cubic zinc blende InN, the elastic components have the following relations

$$C_{11} = C_{22} = C_{33}, C_{12} = C_{23} = C_{31}$$

$$C_{44} = C_{55} = C_{66}, C_s = (C_{11} - C_{12})/2$$

Thus the symmetry has only 3 independent elements: C_{11}, C_{12} and C_{44}, In Table 1, we summarize the calculated elastic constants and bulk modulus of the material InN under 0 Pa. From Table 1, it can be found that except C_{11}, the calculated results are in reasonable agreement with other theoretical work. In order to discuss the pressure dependence of the elastic property, we calculated the elastic contants and bulk modulus in the pressure 0, 10, 20, 30, 40, 50, 60, 70 GPa, and the results were illustrated in Fig. 6. Fig. 6 shows that the elastic components have linear scaling with pressure, C_{11}, C_{12} and B have a positive scaling with pressure, that is, these values increase when the rising of pressure, whereas C_{44} and C_s have a negative scaling. These can also be found from the pressure dependence of the elastic constants in Table 2. The constants C_{11}, C_{12} and B are much larger than C_{44} and C_s, suggesting that the pressure has greater influence on C_{11}, C_{12} and B than on C_{44} and C_s. The obtained results are also in reasonable agreement with those in the work of Kanoum's[13]. For shear modulus pressure dependence, it is shown that when the pressure is about 55 GPa, C_s has a negative value, implying that the InN is unstable. According to reported results[31-32], for zinc blende InN under high pressure, only when the elastic constant tensor components satisfy the following inequality, that is

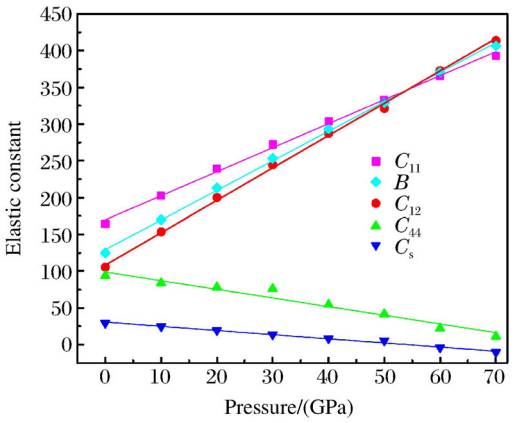


Fig. 6　(Color online) Elastic tensor constants of zinc blende InN as a function of pressure

$$C_{44} > 0,\ C_{11} > |C_{44}|,\ C_{11} + 2C_{12} > 0$$

Then InN crystal will reach dynamical equllibrium, so according to the above criteria, when the

pressure is in the region 0-55 GPa, the InN structure is stable, otherwise it will be unstable.

Table 1 Elastic constants and bulk modulus for InN under 0 pressure

Method	C_{11}	C_{44}	C_{12}	C_s	B
This work	164.23	93.67	105.53	29.35	124.88
Theory[13]	206.57	117.73	112.7	44.135	144
Theory[29]	204	103	102	51	137
Experiment[30]					137

Table 2 Pressure dependence of the elastic constants and bulk modulus of InN

Reference	$\partial C_{11}/\partial p$	$\partial C_{12}/\partial p$	$\partial B/\partial p$	$\partial C_{44}/\partial p$	$\partial C_s/\partial p$
This work	3.45	4.49	4.52	−0.85	−0.51
Ref. [13]	3.852	4.925	4.56	−0.422	−0.536

3.4 The Absorption Spectra of InN

The absorption spectra of InN was shown in Fig. 7. At zero pressure, it can be obviously seen that there are three absorption peaks, which were labeled 1, 2, 3, all these peaks are in the ultraviolet region. At energy 10.7 eV, Peak 3 has the strongest absorption intensity. Peak 1 and Peak 2 have relatively weak intensity, which correspond to the energies 17.2, 21.8 eV, respectively. The corresponding transition should be from the lower valence band to the conduction band, the involved transition electrons could be the In 3*d* or N 2*s* electrons in the lower valence. Since few electrons in lower band can directly reach the conduction, so most electrons have a two step transition: the first step is from the lower valence to the upper valence, and the second is from the upper to the conduction. The two peaks have weak intensities. By comparing the spectra, it can be found that, with the increase of pressure, the absorption peaks move towards the shorter wavelength direction, that is, a blue shift. The shape of the spectra has almost no change when the pressure increases. This is due to the fact that the structure does not have much change, only the lattice constants decrease proportionally with the increase of pressure.

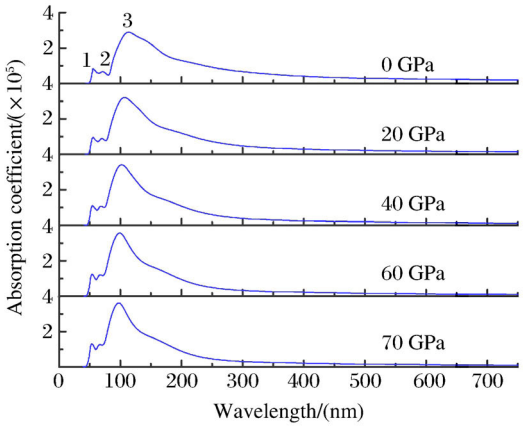


Fig. 7 (Color online) Calculated pressure dependence of the absorption spectra for zinc blende InN

4 Conclusions

We have studied the electronic and optical properties of zinc blende InN under high pressures by means of the first-principles method. It is shown that the lattice constants decrease with increasing pressure. The electrons in the conduction band moves to the higher energy, and the valence band electrons to the lower energy, the energy gap was broadened. The absorption spectrum under pressure has a "blue shift". The elastic constants C_{11}, C_{12}, B, C_s, C_{44} were calculated and the evolution with pressure

was analyzed. It can be found that C_{11}, C_{12} and B increase with the rising of pressure, whereas C_s and C_{44} decrease with increasing pressure. The results are in good agreement with the experimental data.

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高压下闪锌矿 InN 光电性质的密度泛函研究

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摘要: 采用密度泛函理论,计算了闪锌矿型 InN 在压力下的结构、力学性质和光学性质,结果显示,随着压强的增大晶格常数减小。给出了零压下 C_{11}、C_{12}、B、C_s、C_{44} 的值及至 70 GPa 压力下弹性常数随压强的变化关系。结果表明,C_{11}、C_{12}、B 随压强增大而增大,C_s、C_{44} 随压强增大而减小,计算结果与现有实验和理论结果符合较好。在价带区,InN 的分态密度(PDOS)有两个带,且在费米面附近密度很小,显示其倾向于形成稳定结构并且导电性较差。对闪锌矿型 InN 在高压下的光学性质研究发现,导带电子向高能方向偏移,而价带电子向低能方向偏移,结果导致能带间隙增大,光吸收谱在压力的作用发生了"蓝移"。研究结果对认识高压下闪锌矿型 InN 的结构、电学及光学性质具有重要意义。

关键词: 闪锌矿 InN;光电性质;密度泛函理论;高压

中图分类号: O521.2 **文献标识码**: A