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Electronic structure and lattice properties of zinc-blende InN under high pressure

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Abstract. Dependencies of electronic structure and lattice properties of InN with zinc-blende structure on hydrostatic pressure are presented based on band structures computed using the empirical pseudopotential method. The pressure behavior of the pseudopotential form factors have been analyzed. The effect of pressure on the density of states has been examined. Trends in bonding and ionicity under pressure are also discussed. Our results show as well that the absolute value of the Fourier transform of the valence charge density might be useful in the prediction of the phase transition in zinc-blende materials.

PACS. 71.20.-b Electron density of states and band structure of crystalline solids – 71.20.Nr Semiconductor compounds

1 Introduction

The III-V nitrides have attracted strong interest owing to their great potential for the development of opto-electronic devices in the blue and ultraviolet spectral region as well as for high power and high temperature electronics [1–3]. They also have scientific interest, such as the wide differences of fundamental band-gap among them, the luminescence mechanisms, excitons, etc.

Indium nitride (InN) is one of the III-V nitride semiconductors with a large and direct band gap. Good quality indium nitride crystalline thin films have been fabricated on α-Al_2O_3 substrates by various methods [4–6]. InN usually crystallizes as a hexagonal wurtzite lattice [7,8]. Hence, the vast majority of research on InN has been focused on the wurtzite crystal phase. Nevertheless, the recent progress achieved on the growing and doping the materials in the cubic phase has been followed by an interest in studies of structural, electrical and optical properties of zinc-blende InN [3,9,10].

The studies of the pressure behavior of physical properties in semiconductors may provide additional valuable information about these properties. A pressure changes the lattice parameters and, hence, produces shifts of the electronic states in the crystal. Therefore, pressure provides a convenient technique for shifting the relative positions of some energy levels by a controlled amount. It is also evident that by applying sufficient pressure one can change the band extrema from one point of the Brillouin zone to another one. Experimental and theoretical interest in pressure dependence of opto-electronic and structural properties of III-V nitride semiconductors has been growing recently [11–13]. However, these investigations have been much less intense for zinc-blende InN. Thus, further studies of the cubic InN are required to know their basic properties and exploit them in device applications.

In order to provide more information about the physical properties of zinc-blende group-III nitrides, particularly InN, we have computed the electronic and lattice properties of zinc-blende InN using the local model pseudopotential method. The aim of this paper is to examine these properties of InN in the zinc-blende structure, with emphasis on their dependence on hydrostatic pressure.

The plan for this paper is rather straight forward. The method of calculation is succinctly summarized in Section 2. The calculated electronic and lattice properties of the material of interest at various pressures up to 120 kbar are presented and discussed in Section 3. The last section is a brief conclusion.

2 Calculations

The local model pseudopotential method EPM [14] has been employed for the calculations of the studied properties for the material of interest.

If we use a plane-wave expansion for the basis and potential, then the eigenvalue spectrum of the one-electron Schrödinger equation is given by the solution of the secular equation,

$$\det|H(k, G - G') - E(k)I| = 0 \tag{1}$$

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Table 1. Band-gap energies of zinc-blende InN at zero pressure.

Band-gap energy (eV)	
E_0	1.94 [16]
	1.94[a]
E_g^X	2.51 [16]
	2.51[a]
E_g^L	5.82 [16]
	5.82[a]

[a] Present work.

where k is the wave vector, G is a reciprocal-lattice vector,

$$H(k, G-G') = -\left(\frac{\hbar^2 k^2}{2m}\right)\delta_{G,G'} + V(G-G')\,S(G-G') \tag{2}$$

$V(G)$ is the pseudopotential form factor, and $S(G)$ is the structure factor.

In the case of zinc-blende compounds $\mathrm{A}^N\ \mathrm{B}^{8-N}$ we have

$$V(G) = V^S(G)\cos(G\tau) + \mathrm{i}V^A(G)\sin(G\tau) \tag{3}$$

where

$$V^S(G) = \frac{1}{2}[V_A(G) + V_B(G)] \tag{4}$$

$$V^A(G) = \frac{1}{2}[V_A(G) - V_B(G)] \tag{5}$$

$\tau = (a/8)(1,1,1)$, where a is the lattice constant. V^S and V^A are the symmetric and antisymmetric form factors, respectively.

The method of optimisation of the empirical pseudopotential parameters is the non-linear least squares method [15]. However, in the literature, there is a lack of zinc-blende InN experimental data regarding the band structures. Therefore, when the experimental results are not available, our EPM parameters are adjusted to fit the band energies of zinc-blende InN obtained by theoretical calculations at normal pressure (see Tab. 1).

The pressure derivatives of the pseudopotential form factors required in our calculations were determined empirically by fitting the calculated pressure coefficients of certain critical-point band gaps to experimental or theoretical values. In our case, the first-order pressure coefficients of the band gaps (at Γ, X and L) have been fitted to those of reference [13]. The variation of the lattice constant *versus* pressure is calculated using the Murnaghan equation of state [17]. The values of the equilibrium bulk modulus (B_0) and its first pressure derivative (B_0') used in the present work are of 137 Gpa and 4.3 [13], respectively.

Once the band structure has been obtained, the density of states $N(E)$ may be calculated from:

$$N(E) = \frac{1}{NN_a}\sum_k \sum_{n,\sigma} \delta(E - E_{n,\sigma}(k)) \tag{6}$$

where N is the number of primitive cells, N_a is the number of atoms in the primitive cell, and $N(E)$ is normalized to the number of states per atom.

The resulting wave functions $\Phi_{n,k}(r)$ obtained by solving the secular equation of the EPM scheme are used to compute the total valence electron charge density $\rho(r)$ by summing over all the occupied k states of the crystal of the occupied bands n,

$$\rho(r) = 2e\sum_{n,k}^{occ} |\Phi_{n,k}(r)|^2 . \tag{7}$$

3 Results

The final adjusted symmetric and antisymmetric pseudopotential form factors of zinc-blende InN at various pressures up to 120 kbar are given in Table 2. As can be seen from Table 2, all the symmetric pseudopotential form factors of the material of interest are sensitive to the pressure effect. This is not true for all the antisymmetric pseudopotential form factors since we note that $V_A(4)$ is insensitive to the applied pressure, whereas $V_A(3)$ is altered by the pressure effect. The effect of pressure on $V_A(3)$ is not as much as on the symmetric form factors. The situation looks like different for $V_A(11)$. This latter remains constant under pressure until we reach the value of 120 kbar. At this pressure value, $V_A(11)$ changes significantly. Surprisingly, this value is close to that of 12.1 Gpa which represents the experimental transition pressure of InN in the wurtzite structure [13]. The less pressure dependent of the antisymmetric pseudopotential form factors of zinc-blende InN is believed to be due to the high ionicity of the material under consideration.

The lattice constant of InN with zinc-blende structure at zero pressure is taken to be 4.98 Å (9.411 at.units). In Figure 1, we show the variation of the lattice constant of the material of interest as a function of pressure. The lattice constant decreases monotonically with increasing pressure showing a linear behavior according to the following equation:

$$a = 9.41 - 0.0022\ p \tag{8}$$

where the lattice constant a is in atomic units and the pressure p is in kbar.

Figure 2 displays the calculated electron energy band structure of zinc-blende InN at normal and 120 kbar pressure along several symmetry points in the Brillouin zone. The zero energy reference is at the top of the valence band. This latter consists of the triply degenerate Γ_{15} in the absence of the spin-orbit interaction terms in this work. The upper valence bands are derived from the p orbital of N and with some admixture of the p orbital of the cation In. The first conduction band at Γ is predominantly of cationic s character. The results show that at zero pressure, the material under investigation is a direct-gap semiconductor with the minimum of conduction band at Γ point. The width of the energy gap between the highest level of the valence bands at Γ and the

Table 2. Symmetric and antisymmetric form factors in Ry of zinc-blende InN at various pressures.

Form factors	$P = 0$ kbar	$P = 30$ kbar	$P = 60$ kbar	$P = 90$ kbar	$P = 120$ kbar
$V_S(3)$	–0.172195	–0.205838	–0.217258	–0.219582	–0.211053
$V_S(8)$	–0.01555	–0.017804	–0.025602	–0.033525	–0.042874
$V_S(11)$	0.044698	0.048052	0.060946	0.074095	0.025957
$V_A(3)$	0.238742	0.209993	0.203944	0.207506	0.222535
$V_A(4)$	0.23210	0.232100	0.232100	0.232100	0.232100
$V_A(11)$	–0.03149	–0.031490	–0.031490	–0.031490	–0.094526

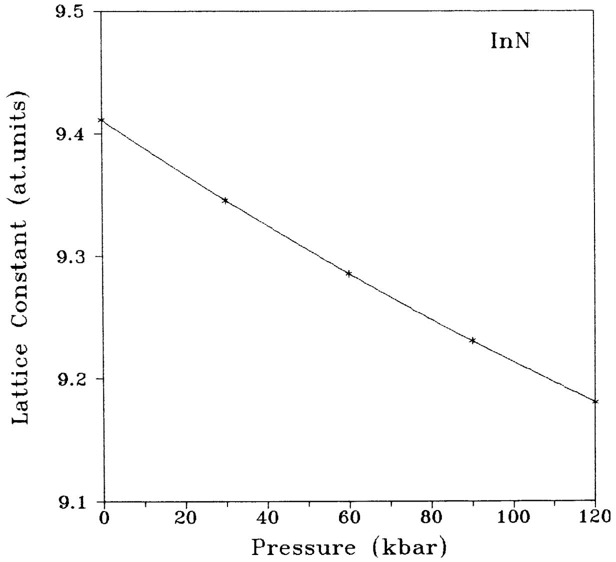


Fig. 1. Lattice constant of zinc-blende InN as a function of pressure.

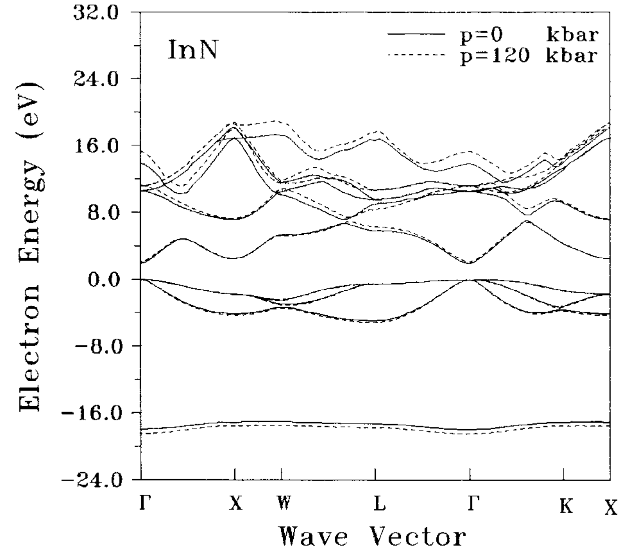


Fig. 2. Band structure for zinc-blende InN.

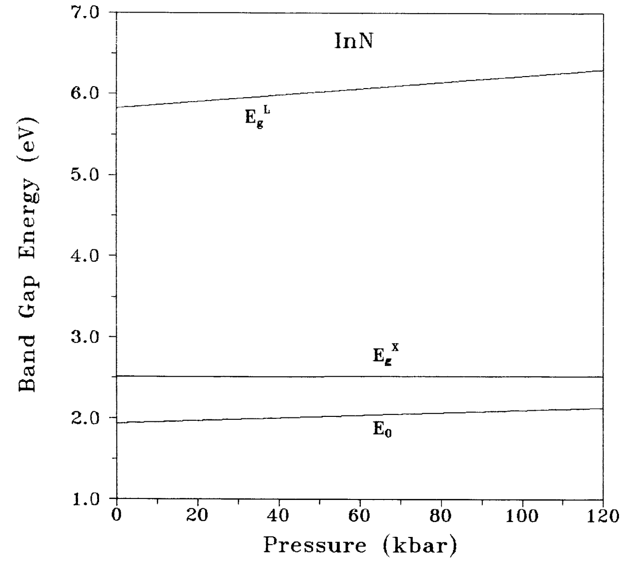


Fig. 3. Direct and indirect band gaps in zinc-blende InN as a function of pressure.

lowest one of the conduction bands is 1.94 eV. Qualitatively, the overall shapes of the valence bands are almost similar to those found by Christensen and Gorczyca [13] for zinc-blende InN using self-consistent linear muffin-tin-orbital band-structure calculations. Generally, the main difference between the valence band structure of zinc-blende and wurtzite crystals is the absence of the crystal field splitting in the zinc-blende structure due to the cubic symmetry [3]. Applied pressure affects the electronic band structure of zinc-blende InN, although the shape of the bands remains almost the same as at normal pressure (Fig. 2, dashed line). Practically, all the valence bands are slightly shifted downwards. Consequently, the full valence band width (VBW) increases with increasing pressure indicating therefore a decrease of the ionicity character of the studied material. This is consistent with the behavior of the ionicity in semiconductors under pressure. However, the shift of the conduction bands depends on the k point and energy. The $E_0(\Gamma^c - \Gamma^v)$ band-gap energy (where the superscripts c and v on the level notation refer to the conduction and valence bands, respectively) increases from 1.94 eV at normal pressure to 2.13 eV at 120 kbar pressure, whereas, $E_g^X(X^c - \Gamma^v)$ and $E_g^L(L^c - \Gamma^v)$ increase from 2.51 and 5.82 eV at zero pressure to 2.52 and 6.30 eV at 120 kbar pressure, respectively. We do expect therefore that the zinc-blende InN remains a direct band gap over the pressure range from 0 up to 120 kbar. This is clearly seen in Figure 3.

Often people present the variation of the energy-band gaps as a function of $\frac{\Delta a}{a_0}$ (where $\Delta a = a_p - a_0$ and a_p and a_0 are the lattice constants at pressure p and at zero

Table 3. Calculated pressure coefficients of the main band gaps (b^* and c^* are in eV) for zinc-blende InN.

Band-gap	b^*		c^*	
	Present work	Ref. [12]	Present work	Ref. [12]
E_0	–6.87	–15.27	33.14	–30.71
E_g^X	–0.37	–5.19	3.14	–39.05
E_g^L	–16.23	–20.07	137.74	–37.39

pressure, respectively). By simply combining the relationships (8) plotted in Figure 1 and those shown in Figure 3, the dependencies of the E_0, E_g^X and E_g^L band gaps for zinc-blende InN on $\frac{\Delta a}{a_0}$ have been obtained according to the following relation,

$$E = a^* + b^* \left(\frac{\Delta a}{a_0}\right) + c^* \left(\frac{\Delta a}{a_0}\right)^2 \cdot \qquad (9)$$

The resulting pressure coefficients b^* and c^* from the quadratic fits are given in Table 3. Other theoretical estimates reported in reference [12] are also presented. Our results do not agree with those of reference [12]. This discrepancy is quite expected because the energy band-gaps at the principal symmetry points of the Brillouin zone at normal pressure and their first-order pressure coefficients have been fitted to those of reference [13] that are in disagreement with those of reference [12]. On the other hand it should be noted that all the dependencies of the E_0, E_g^X and E_g^L on $\frac{\Delta a}{a_0}$ obtained by our calculations as well as by reference [12] show a non-linear behavior.

Figure 4 shows the density of states (DOS) for zinc-blende InN. The zero point of energy is taken to be at the top of the valence band. The threshold of the valence-band contributions to the density of states for the material of interest is approximately ≈ -18 eV below the top of the valence band, and occurs at $\Gamma_1(M_0)$. The density of the lowest valence band from ≈ -17.8 to ≈ -16.5 eV has primarily s character and is localized on the anion. The main peak at ≈ -17 eV comes from the entire square face of the Brillouin zone which turns out to be a surface of nearly constant energy which agree with the DOS of other III-V semiconductors [18]. We notice a ≈ 11.7 eV gap between the first and the second valence bands. The gap extends from ≈ -16.5 to ≈ -4.8 eV. This is not true for Si and Ge where it has been found that this gap is zero [18]. This can be well understood by the fact that this gap is related to the antisymmetric form factors, $V^A(G)$ which are for zinc-blende InN no longer zero as in the case of Si and Ge. The density of the second valence band is primarily of cation s character and it changes rapidly to anion p-like at the top of the valence band. The upper part of the valence band consists mainly of N $2p$ states hybridized with In $5p$ states. All of the valence s and p states of In and N atoms contribute to the formation of the conduction band edges-with-s-like states being a bit more significant. The free-electron behavior of conduction-band densities of states results in more dispersive bands, band crossings, and many Van Hove singularities. Due to its strong dispersion, the DOS of the conduction band is much smaller than that of the highest valence bands. It is clear that the applied pressure does not give essential changes in the shape of the DOS curve. However, from the quantitative point of view, we note that the threshold of the lowest valence band is shifted to occur approximately at –18.19 eV at $\Gamma_1(M_0)$ On the other hand, the peaks of DOS generally move downward as the pressure increases, meanwhile the full valence band width becomes wider indicating once again the decrease of the ionicity of the material under consideration. Another trend observed in the calculated density of states is that generally the widths of the various peaks increases as the compound becomes less ionic. The DOS of the conduction bands is also altered by the pressure effect where changes in the relative positions of the conduction bands with respect to the top of the valence band are clearly seen.

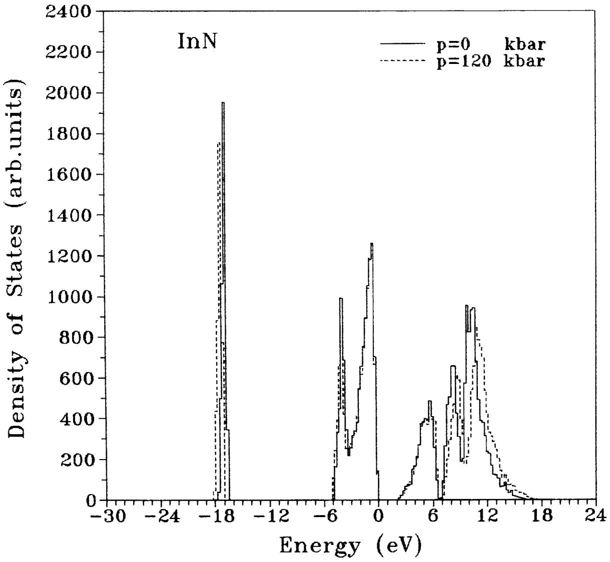
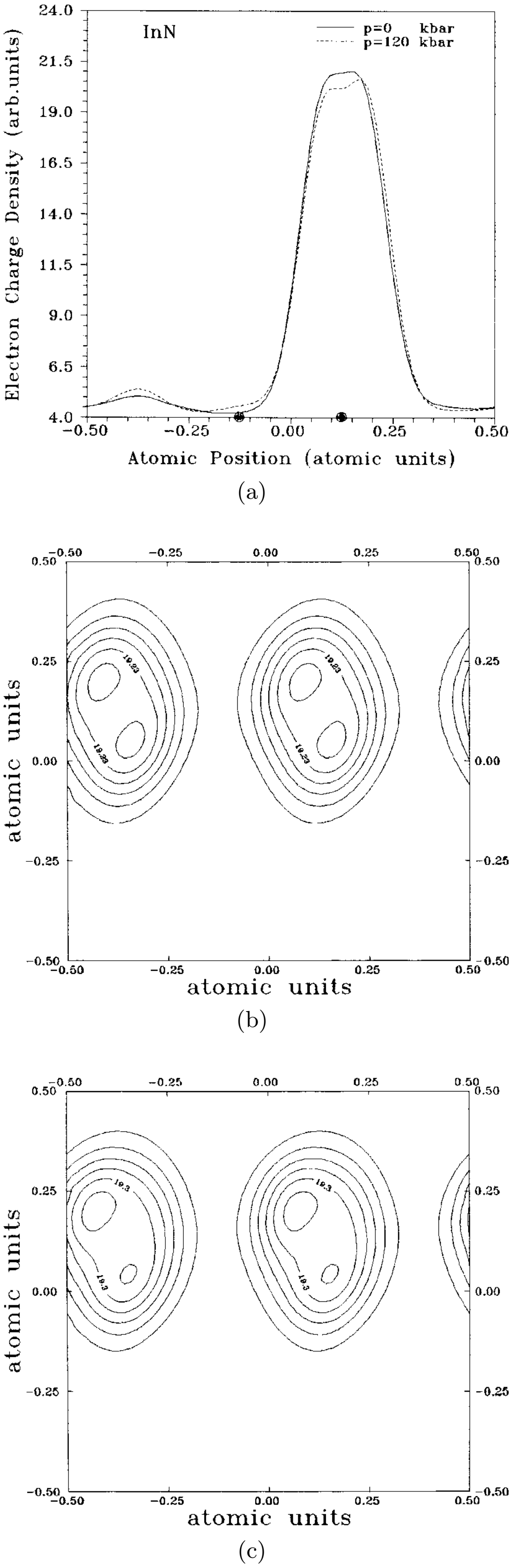


Fig. 4. Density of states for zinc-blende InN.

The calculated band structure makes it possible to theoretically determine zinc-blende InN charge density. Hence, the total valence electron charge density was computed along the [111] direction and in the (110) plane for zinc-blende InN at normal and 120 kbar pressure by using the special point scheme of Chadi and Cohen [19], with $k_1 = (\frac{2\pi}{a})(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ and $k_2 = (\frac{2\pi}{a})(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, where a is the lattice constant, through the relation (7), with $n = 1$ to 4. As can be seen from the profiles and contour plots of Figure 5, at zero pressure, the center of the bonding charge has moved towards the N ion. This is an indication of the strong ionic character of the bonding between In and N atoms. Practically, there is no charge density in the interstitial region nearest to the anion (N), whereas we note a small amount of charge density in the interstitial region nearest to the cation (In). While the shape of the profile of zinc-blende InN resembles qualitatively that of HgTe [20] it differs and so in regard to details from those of III-V binary compounds [21] and ternary semiconductor alloys [22]. This discrepancy is though to be an immediate consequence of the difference in the corresponding



(a)

(b)

(c)

Fig. 5. Total valence charge density (a) along the [111] direction (b) in the (110) plane: at zero pressure and (c) in the (110) plane: at 120 kbar pressure, for zinc-blende InN using the two point scheme of Chadi and Cohen.

Table 4. The absolute values of the Fourier transform of the valence charge density for zinc-blende InN at various pressures.

Pressure (kbar)	$\lvert\rho(222)\rvert$
0	0.01595959
30	0.03889138
60	0.05209547
90	0.06143402
120	0.00305902

ionicities. Under hydrostatic pressure, although the topology of the valence density (profiles and contours) in zinc-blende InN is not completely changed, we can note that the maximum of the charge density of valence electrons that gives the main contribution to the formation of chemical bond decreases and becomes less flat. A slight de-enhancement of the charge density is noticed in the interstitial region nearest to the anion (N), accompanied by a small increase in the interstitial region nearest to the cation (In). A decrease of the charge at the anion site accompanied by an increase at the cation one is also observed. All these fact leads us to believe that the ionic character of the material of interest becomes weaker when this latter is compressed.

It has been proposed that the X-ray intensity at the forbidden 222 reflection is useful as an order parameter in the phase transition from a diamond-like semiconductor to a metal [23]. In zinc-blende materials the 222 components of the valence charge densities may be considered to contain contributions from two sources, the bond charges and charge build-ups about the anion. In Table 4, we give the absolute values of the Fourier transform ($\rho(222)$) of the valence charge density at some pressures up to 120 kbar. It should be noted that before reaching the pressure of 120 kbar, the absolute value of $\rho(222)$ increases monotonically with increasing pressure. However, at 120 kbar pressure, it decreases rapidly. This surprisingly corresponds to the observed pressure transition of InN with wurtzite structure [13], which can predict that a structural change may have occurred in the vicinity of 120 kbar. We state then that the absolute value of $\rho(222)$ might be a good tool for the prediction of the phase transition in zinc-blende InN. Further studies for other zinc-blende materials are clearly required to confirm this.

4 Conclusion

Electronic and lattice properties of InN in the zinc-blende structure are calculated using the empirical pseudopotential method. A summary of the key findings follows: (i). The antisymmetric pseudopotential form factors are less pressure dependent. This behavior is thought to be due to the high ionicity of the material of interest. (ii). Although the electronic band structure is affected by pressure, it is expected that the zinc-blende InN remains a direct band gap in the pressure range 0 to 120 kbar. (iii). The direct and indirect band gaps (at Γ, X and L) are found to vary non-linearly with $\frac{\Delta a}{a_0}$. (iv). Although no essential changes in the shape of the density of states are observed, the full valence band width becomes wider indicating thus the decrease of the ionicity character in the material under consideration under hydrostatic pressure. (v). The profiles and contour maps of the total valence charge density shows a strong ionic character of the bonding between In and N atoms. This ionic character becomes weaker when pressure is applied. (vi). Finally, it is proposed that the absolute value of the Fourier transform ($\rho(222)$) of the valence charge density is useful in the prediction of the phase transition in zinc-blende materials.

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