Structural, electronic, and optical properties of wurtzite and rocksalt InN under pressure

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Structural stability, electronic, and optical properties of InN under high pressure are studied using the first-principles calculations. The lattice constants and electronic band structure are found consistent with the available experimental and theoretical values. The pressure of the wurtzite-to-rocksalt structural transition is 13.4 GPa, which is in an excellent agreement with the most recent experimental values. The optical characteristics reproduce the experimental data thus justifying the feasibility of our theoretical predictions of the optical properties of InN at high pressures.

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Indium nitride (InN) is a promising material for technological developments because of a very narrow direct band gap, superior carrier transport characteristics and electrical conductivity in a wide range of temperatures.1 Under high pressures, InN experiences phase transitions from the wurtzite-to-rocksalt structure.2 However, there are significant discrepancies between the transition pressures reported in theoretical3–5 and experimental studies.6–10 Moreover, since the properties of InN are sensitive to external pressure, exploring the electronic and optical properties of InN under high pressures is important.

Here, we study the structural, electronic and optical properties of wurtzite and rocksalt InN under high pressure. The results are in a good agreement with the recent experimental and theoretical data. We also predict the optical characteristics of InN at high pressures.

We have used the first-principles pseudopotential plane-wave method based on the density-functional theory (DFT) incorporated into the CASTEP computational code. Ultrasoft pseudopotential with \(4d^{10}5s^{2}5p^{1}\) and \(2s^{2}2p^{6}\) valence-electron configurations for In and N atoms, respectively, were used. The exchange and correlation potentials are described in the framework of the generalized gradient approximation (GGA) and the local-density approximation (LDA). In the wurtzite InN, the In and N atom positions are \(\text{In}(0,0,0)\), \(\text{In}(1/3,2/3,1/2)\), \(\text{N}(0,0,u)\), and \(\text{N}(1/3,2/3,u+1/2)\), where \(u\) is a dimensionless parameter that represents the distance between the In plane and its nearest-neighbor N plane, expressed in the units of the lattice parameter \(c\). On the other hand, the In and N atom positions in the rocksalt InN structure are \(\text{In}(0,0,0)\), and \(\text{N}(1/2,1/2,1/2)\), respectively. The plane-wave cutoff energy was assumed to be 750 eV, while the Brillouin-zone sampling mesh parameters for the k-point set were chosen as \(12 \times 12 \times 6\) and \(12 \times 12 \times 12\) for the wurtzite and the rocksalt phases of InN, respectively. The maximum magnitudes of the forces on the atom, stress, and atomic position displacement between computational cycles were maintained below 0.01 eV/Å, 0.02 GPa, and \(5 \times 10^{-4}\) Å, respectively.

To confirm the transition pressure between the wurtzite and rocksalt structural phases of InN, we have calculated the Gibbs free energy \(H=E+PV+TS\) for the two phases. The \(E-V\) and \(G-P\) curves are shown in Fig. 1. The transition pressure \(P_t\) deduced from either the \(E-V\) or \(G-P\) curves are

![Figure 1](image_url)

FIG. 1. (Color online) The energy as a function of volume, the inset is the Gibbs energy as a function of pressure for both wurtzite and rocksalt structural phases of InN calculated in the framework of (a) GGA and (b) LDA.
approximately 13.4 GPa for GGA and 10.2 GPa for LDA
cases. Our result obtained using the GGA is in an excellent
agreement with the most recent experimental value
13.5/11006
0.5 GPa measured by Raman scattering.9 Compared
to the LDA-predicted values calculated in this work
10.2
20851
10.2
20849
10.86 GPa3
20849
11.1 GPa5
20850
indicating that the calculations based on the
GGA are much more accurate to predict the phase-transition
pressure.3,11 This fact will also support the validity of our
theoretical predictions of other properties of InN under high-
pressure conditions.

The computed values of the lattice constants as a function
of pressure are plotted in Fig. 2; all the lattice constants
decrease as the pressure increases. The equilibrium lattice
constants \(a_0\) of wurtzite and rocksalt structure are 3.583
and 4.712 Å at normal (zero external) pressure, respectively, in
accordance with the values calculated by other authors.3,12,13
The calculated lattice constants of wurtzite InN at zero ex-
ternal pressure are in an excellent agreement with the experi-
mental results.7 Even at 20 GPa, the calculated value
(4.562 Å) of rocksalt InN still exhibits a very good agree-
ment with the experimental value 4.535 ± 0.001 Å obtained
by x-ray diffractometry.6 Figure 3 shows the dependence of
the relative volume of the wurtzite and the rocksalt InN
phases on the external pressure. The relative volume de-
creases almost linearly with the pressure, reasonably close to
the experimental data.6,7

Figure 4(a) shows the band structure of the wurtzite InN
phase with and without the external pressure of 13.4 GPa.
Under no-external-pressure conditions, an almost zero direct
band gap can be observed at a highly symmetric \(\Gamma\) point,
close to the theoretical value,14 yet smaller than the experi-
mental value reported.15 This underestimate, which is very
common to most of the DFT approximations,11,16 can be re-
duced by using the energy scissor approximation.17,18

From the band structure of the rocksalt InN under 13.4
and 40 GPa shown in Fig. 4(b), one can note that the
conduction-band minimum is located at the \(\Gamma\) point, while
the valence-band maximum is located at the \(L\) point, indicat-
ing that the rocksalt InN is an indirect band-gap semiconduc-
tor. The topmost electron levels of the valence band are
threefold degenerate at the \(\Gamma\) point, and twofold degenerate
at the \(L\) and \(X\) points. When the pressure increases, the va-
ence band tends to broaden and shift toward the lower-
energy region whereas the conduction-band levels shift to-
ward the higher-energy region for both low- and high-
pressure structural phases. Indeed, interatomic spacing is
expected to decrease as the pressure becomes higher. Under
such conditions, the wave functions overlap more strongly.
Thus, there is an increase in the dispersion of the bands in \(k\)
space as well as in the bandwidths. Hence, the band gap
broadens at higher pressures.

In Fig. 5, the distribution of the density of states of the
wurtzite and the rocksalt InN over the energy spectrum is
presented. The valence band can be divided into two zones.
The lower part of the valence band (from −16.5 to appro-
nately −10.0 eV) is mostly composed of \(\text{In} 4d\) and \(\text{N} 2s\) states, where the \(\text{In} 4d\) states exhibit quite strong localiza-
tion. On the other hand, the upper part of the valence band
(from −7.5 to 0.0 eV) contains \(\text{N} 2p\) states coupled with
\(\text{In} 5p\) and \(\text{In} 5s\) states. The most prominent unoccupied en-
ergy bands in the lowest energy domain of the conduction

FIG. 2. (Color online) The variation in the lattice constants ver-
sus pressure for wurtzite and rocksalt InN.

FIG. 3. (Color online) Changes of the relative volume of wurtz-
ite and rocksalt InN with increasing pressure. The squares are this
work; the triangles and stars from Refs. 6 and 7, respectively.

FIG. 4. (Color online) Band structure: (a) wurtzite InN under 0
and 13.4 GPa (b) rocksalt InN under 13.4 and 40 GPa.
The range between 5 and 7 eV. Above this range, the spectrum exhibits a small blueshift for the wurtzite InN without any external pressure. The peak at 5.3 eV takes its origin from the optical transitions between N 2p states in the valence band and In 5p states in the conduction band, while the other peak at 10.0 eV is caused by the optical transitions from 5p and 5s states of In to N 2p states. When the pressure increases from 0 to 13.4 GPa, the spectrum exhibits only one negative region in the range of 10–12 eV.

The refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ have also been calculated for wurtzite InN under 0 and 13.4 GPa and the rocksalt InN under 13.4 and 40 GPa external pressures, as displayed in Figs. 6(c) and 6(d), respectively. For wurtzite InN under no-external-pressure conditions, the static refractive index is $n_0=2.7$. Moreover, $n_0$ of both wurtzite and rocksalt InN decreases as the pressure increases. The $k(\omega)$ shows two main peaks at around (5.9 and 11.2 eV) and (6.4 and 11.7 eV) for the wurtzite and the rocksalt InN at 13.4 GPa, respectively. For the wurtzite InN, the peak intensity at around 6.4 eV is stronger than that at ~5.9 eV. Both the refractive index and the extinction coefficient shift toward the higher-energy region when the pressure increases.

We stress that at high pressures the refractive index of InN in the 2.8–7.3 eV range is up to 2 times higher than under normal conditions. The extinction coefficient, in turn, decreases in the 2.6–5.1 eV range and increases in the 5.1–7.5 eV range. One can thus expect much stronger refraction and much weaker damping of the light with photon energies between 2.8 and 5.1 eV.

In conclusion, we studied the structural stability, electronic band structure, electronic density of states, and optical properties of wurtzite and rocksalt InN under pressure. The calculated lattice constant and the transition pressure are in a very good agreement with the experimental results. The wurtzite InN is a direct band-gap semiconductor, while the rocksalt InN is an indirect band-gap semiconductor. As the pressure increases, the valence-band levels shift toward the lower-energy domain whereas the conduction-band levels shift toward the higher-energy region. This allowed us to predict the variation of the optical properties for the rocksalt or wurtzite InN under pressure.
17. Underestimates of the optical band-gap values are common to either LDA or GGA. The scissor operation is reasonably accurate for the prediction of the optical properties of InN. More advanced methods such as GW quasiparticle method (Ref. 19) or DFT+$U$ (Ref. 20) could possibly improve the accuracy.