DFT STUDIES ON ELECTRONIC STRUCTURE AND ELASTIC PROPERTIES OF CoN: ZINCBLENDE AND ROCKSALT STRUCTURES

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ABSTRACT

We have calculated *ab initio* the electronic, structural and elastic properties of CoN in rocksalt (RS) and zincblende (ZB) structures using full potential linearised augmented plane wave method with generalised gradient approximation as exchange correlation. Of these two phases, the ZB-CoN is more stable. The density of states show no band gap indicating the compound is metallic. The second order elastic constants have been calculated and other related quantities such as Zener anisotropy factor, Poisson's ratio, Young's modulus, Kleinman parameter, Debye temperature, sound velocities have also been determined.

Key words: DFT; electronic structure; DOS; elastic constants

Introduction

Transition metal nitrides are well known for possessing a number of extreme properties that are of scientifically interest and technologically important [1]. They show a rich variety of properties ranging from high T_c superconductivity to very hard surface coatings and heterogeneous catalysis. In view of these properties, a large number of theoretical investigations were carried out in the last few decades [2-4]. The aim of this paper is to present the result of a theoretical investigation of the structural, electronic and elastic properties of CoN in both rocksalt and zincblende structures. The calculations were done using the full-potential linearised augmented plane wave (FP-LAPW) method [5-7] based on the density functional theory. Recently CoN has been synthesized by Suzuki et al in zincblende structure [8]. In addition, Taylor et al. [9] reported the existence of CoN in zincblende structure. Schmit-Dumont et al.[10] synthesized CoN in rocksalt structure. However, Shimizu's [4] theoretical calculation using LDA claimed that rock salt structure is more stable. While Wang Hong Bo et al.[11], using GGA, have shown that ZB-CoN is more stable. From the earlier comparisons [12-14] of the computational works using LDA and GGA, it is well known that GGA yields good agreement with experiments. Therefore, in this study, GGA is applied. The rest of the paper is organised as follows. In sec. 2 we describe the details of the *ab initio* method used. In sec. 3 we report the structure of two different phases of CoN studied band structure, density of states and elastic constants of RS-CoN and ZB-CoN as results and discussion. Overall conclusion is given in sec.4.

Computational details

The calculation of cobalt nitrides in the rock salt and zincblende structures were performed with the FP-LAPW within the framework of the density functional theory with GGA-PBE for the exchange correlation potential [5]. We have employed the scalar relativistic hybrid full potential (linearized) augmented plane waves plus local orbitals (FP-LAPW+lo) method as implemented in the WEIN2k code.[15]. This method has been extensively tested and is among the most accurate methods for performing electronic structure calculations of crystals. In this method, the unit cell is devided into non-overlapping atomic

spheres whose centre is at atomic position and interstitial region. Inside the muffin tin region the potential is a product of radial function and spherical harmonics. For the interstitial region, i.e., outside the muffin tin sphere, the potential are expanded in plane waves. Muffin-tin spheres for metal atoms, carbon atoms and nitrogen atoms are listed in table 1.For every case the wave functions inside the MT spheres which are expanded into spherical harmonics are up to $l=9$ and the $RK_{max}=10$. The number of k points used for the integration procedure is 7000 which reduces to 222 irreducible k points inside the Brillion zone including five high symmetry points W, L, Γ, X and K. The calculations were performed at the equilibrium lattice constants, which are determined from the plot of total energy against the unit cell volume by fitting to the Murnaghan equation of state [16].

Results and Discussion

We investigated two different phases of CoN, namely, the rock salt structure (space group F-43m) and zincblende structure (space group Fm-3m). The equilibrium lattice parameter, bulk modulus, and its pressure derivative have been computed by minimizing the crystal total energy calculated for different values of the lattice constants by means of Murnaghan's equation of state (EOS) [16] and are shown in Fig 1 (a)-(b). The results are listed in Table 1 along with other experimental and theoretical values. It is found that zincblende (ZB-CoN) phase has lower energy and is more stable structure. This result is not in agreement with the other theoretical work by Schimizu et al. which claimed that RS-CoN is more stable than ZB-CoN. The lattice parameters are found to be 4.00 Å for RS-CoN and 4.24 Å for ZB-CoN. It indicates that the unit cell of RS-CoN is smaller than that of ZB-CoN, which is in agreement with the experimental result. The lattice parameter of ZB-CoN differs from that of experimental by an amount of 0.04 Å to 0.05 Å, indicating the accuracy of our work. The calculated bulk moduli fo RS-CoN and ZB-CoN are 3.09 Mbar and 2.58 Mbar respectively which are in agreement with other theoretical work by Wang Hong-Bo et al [11]. The band structure of CoN in both structures are shown in Fig.2(a)-(b). It can be seen that there are many bands crossing the Fermi level in the band structures of

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both structures. It clearly indicates that RS and ZB structure of CoN exhibits metallic in nature. The total and partial density of states (DOS) are shown in Fig. 3 (a-f). The metal 3d states and the N 2p states are strongly hybridized in total DOS in both the structures. The lowest band in the band structure is mainly nitrogen 2s orbital. They do not contribute to the bonding. Above this band, there lies the 2p non-metal and 5d metal states. These bands overlap and mixed in Δ. According to Hund's rule, the d band is further decomposed to d-t_{2g} and d-e_g. This is observed in band structure as the 3d metal state decomposes to d-t_{2g} and d-e_g originating at Γ. The bands near the Fermi level are mainly contributed by Co-d and N-p.

From the valence electron density plot along the 100 planes in Fig.4 (a) and Fig. 4(b), it seems that the bond between the Co and N in RS-CoN has more covalent nature whereas ZB-CoN shows more ionic nature. This may be the cause of difference in stability and other physical properties such as hardness etc. The covalency/ionicity nature in the compound can also be explained from charge tranfer analysis.

The difference in the electronic charge inside the atomic sphere between the crystal (LAPW) value $Q_{crystal}^{sphere}$ and the superimposed atomic value $Q_{crystal}^{sphere}$ which is the quantity for studying charge transfer in a compound are given in table 2. From this table we can observe that in ZB-CoN there is a charge transfer of about two electrons from the metal to the non-metal. While in RS-CoN the charge transfer is about half an electron. Therefore one can conclude that ionic nature is more in ZB-CoN where as covalent nature is more in RS-CoN.

In this study, to compute the elastic constants C_{ij}, we use the 'volume conserving' technique [17]. For cubic crystal structures such as those of ZB-CoN or RS-CoN, the necessary condition for mechanical stability is given by [18] $(C_{11}-C_{12}) > 0$, $(C_{11}+2C_{12}) > 0$, $C_{11} > 0$, $C_{44} > 0$. The findings are listed in Table 1. These values satisfy all the stability conditions. Thus we have concluded that both ZB-CoN and RS-CoN are mechanically stable which favours the experimental results [8-10].
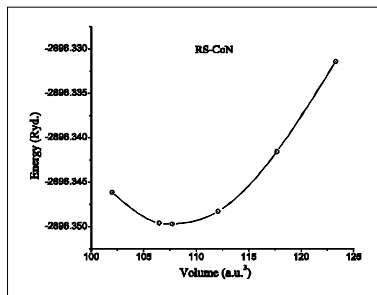

Fig.1 (a) Total energy of RS-CoN as a function of volume. The circles are the calculated points and the curve is fitted to Murnaghan's equation of state.
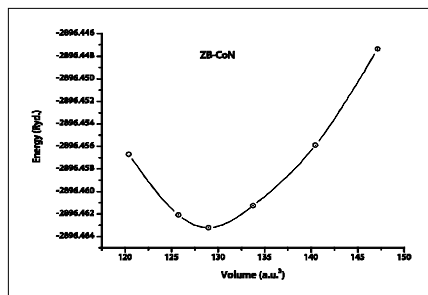

Fig. 1(b) Total energy of ZB-CoN as a function of volume. The circles are the calculated points and the curve is fitted to Murnaghan's equation of state.
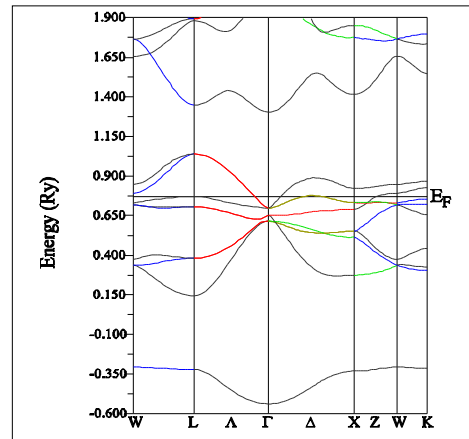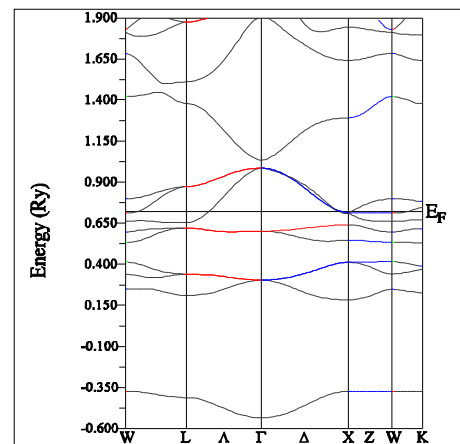

Fig.2. (a) Electronic band structure of RS-CoN
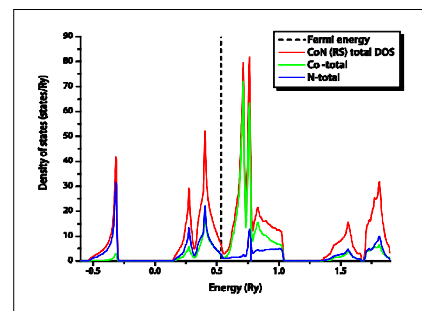

Fig.2. (b) Electronic band structure of ZB-CoN

Fig. 3. (a) Total density of states of RS-CoN
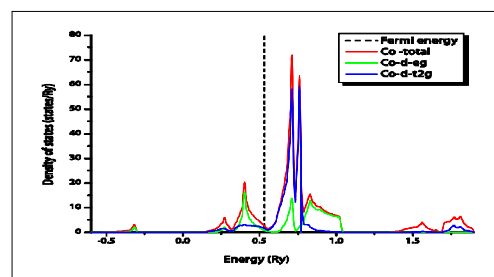

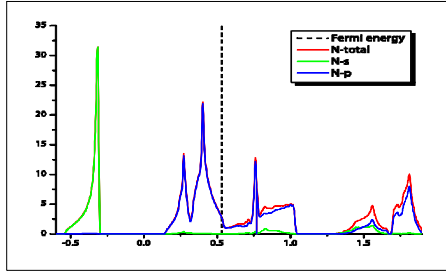**Fig. 3. (b).** Partial density of states of Co in RS-CoN

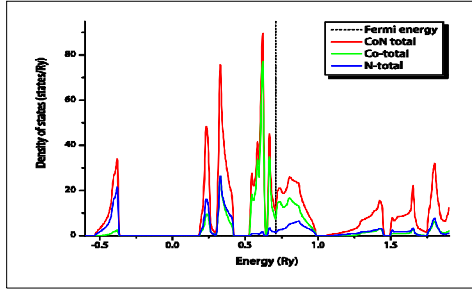**Fig. 3 (c)** Partial density of states of N in RS-CoN.

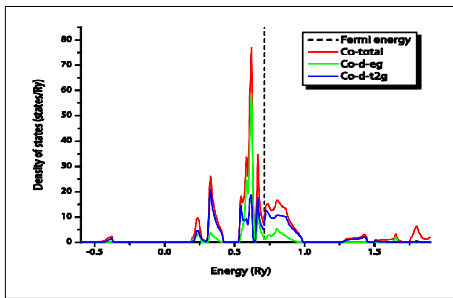**Fig. 3 (d)** Total density of states of ZB-CoN

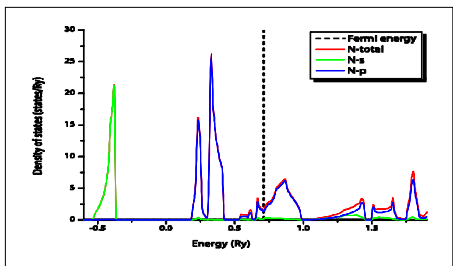
Fig. 3 (e) Partial density of states of Co in ZB-CoN

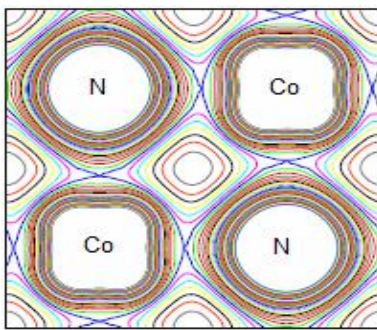
Fig. 3. (f) Partial density of states of N in ZB-CoN.

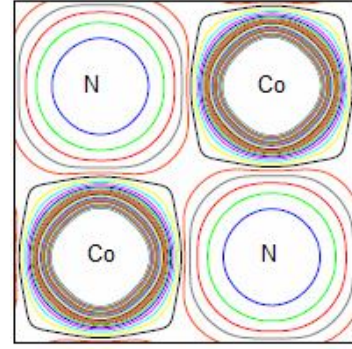**Fig. 4. (a)** Total valence charge density of RS-CoN in 100 plane.

Fig. 4. (b) Total valence charge density of ZB-CoN in 100 plane

Table 1. Calculated and experimental lattice constant (a0), bulk modulus (B), and the pressure derivative of bulk modulus (B'), Zener anisotropy factor (A), Poisson's ratio (ν), Kleinman parameter (ζ), Young's modulus (Y), and shear modulus (C'), longitudinal, transverse, average elastic wave velocities (vl ,vt ,vm) and the Debye's temperature (θD) of RS-CoN and ZB-CoN.

Parameters	Rock salt structure	Zincblende structure
a_0 Å	4.00 [a], 4.05 [b], 3.90 [c], 4.27 [d]	4.24 [a], 4.29 [b], 4.20 [c], 4.296 [f], 4.428 [g]
B Mbar	3.09 [a], 2.93 [b], 4.82 [c]	2.58 [a], 2.56 [b], 2.45 [c]
B'	4.51 [a]	8.06 [a]
C_{11} Mbar	4.36 [a]	2.77 [a]
C_{12} Mbar	2.87 [a]	2.08 [a]
C_{44} Mbar	0.99 [a]	1.45 [a]
A	1.34 [a]	4.19 [a]
ν	0.37 [a]	0.36 [a]
ζ	0.75 [a]	0.82 [a]
Y (Mbar)	2.43 [a]	2.22 [a]
C'(Mbar)	0.74 [a]	0.34 [a]
v_l (m/s)	10620.50 [a]	10764.12 [a]
v_t (m/s)	4840.97 [a]	5086.85 [a]
v_m (m/s)	5456.72 [a]	5724.03 [a]
θ_D (K)	644.93 [a]	637.34 [a]

a Present work, b Ref. [11], c Ref. [4], d Ref. [9], e Ref. [22], f Ref. [8]

Table 2 LAPW partial charge difference for RS- CoN and ZB-CoN

	RS- CoN		ZB-CoN	
Inside the atomic spheres	Co	N	Co	N
$Q_{crystal}^{in}$	25.016	6.568	24.432	5.654
Q_{atomic}^{in}	25.061	6.225	26.431	5.653
$Q_{crystal}^{in}$ - Q_{atomic}^{in}	-0.448	0.343	-1.999	0.001

The Zener anisotropy factor A, Poisson's ratio ν, shear modulus C', and Young's modulus Y are calculated using the relations given by Mayer et al. [19].

$$A = \frac{2C_{44}}{C_{11}C_{12}} \qquad \nu = \frac{1}{2}\left[\frac{B - \frac{1}{2}G}{B + \frac{1}{3}G}\right], \qquad Y = \frac{9GB}{G + 3B}$$

Where, $G = G_V + G_R /2$ is the isotropic shear modulus, GV is Voigt's shear modulus corresponding to the upper bound of G values, and GR is Reuss,s shear modulus corresponding to the lower bound of G values. They can be expressed as

$$G_V = \frac{(C_{11} - C_{12} + 3C_{44})}{5}$$

$$\frac{5}{G_R} = \frac{4}{(C_{11} - C_{12})} + \frac{3}{C_{44}}$$

The Kleinman parameter ζ which describes the relative positions of the cation and anion sub lattices under volume conserving strain distortions for which positions are fixed by symmetry. We use the following relations

$$\zeta = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}}$$

for Kleinman parameter and

$$C' = (C_{11} - C_{12})/2$$

for the shear modulus [20]. The calculated value of density ρ, Zener anisotropy factor A, Poisson's ratio υ, Kleinman parameter ζ, Young's modulus Y, and shear modulus C' of RS-CoN and ZB-CoN are listed in table 1. Following common relation given in Ref. [21], the Debye temperature θD is calculated from the elastic constants data using the average sound velocity vM, by the relation

$$\theta_D = \frac{h}{k} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} \nu_M$$

where h is Plank's constant, k is the Boltzmann's constant, NA is Avogadro's number, n is the number of atoms per formula unit, M is the molecular mass per formula unit, ρ (=M/V) is the density, and vM is given as [23]

$$\nu_M = \left[\frac{1}{3} \left(\frac{2}{\nu_t^3} + \frac{1}{\nu_l^3} \right) \right]^{\frac{1}{3}}$$

where vl and vt are the longitudinal and the transverse elastic wave velocities, respectively, which are obtained from Navier's equations [24]

$$\upsilon_l = \sqrt{\frac{3B + 4G}{3\rho}} \qquad \upsilon_t = \sqrt{\frac{G}{\rho}}$$

The calculated values of the longitudinal, transverse and average sound velocities along with the Debye temperature are given in Table 1.

Conclusion

To conclude, we have studied the structure, elastic properties, and lattice stability of CoN in rock salt and zincblende phase. The calculation reveals that with two structures, the ground state energy of zincblende phase of CoN is higher as compare to rock salt CoN phase. The calculated band structure shows that these materials are metallic in nature. The density of states for both structures indicate that the metal Co 3d state intensely hybridize with the N 2p. The bonding nature of RS-CoN can be described as covalent due to hybridization of N and Co states, but there is also some ionic character with the electron transfer from the metal atoms to nitrogen atoms as well as obvious metallic

character. The bonding nature of RS-CoN is seems to be dominated by covalent nature and that of ZB-CoN is dominatd by ionic nature.

Acknowledgments

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