

A DFT Study on Electronic Structures and Elastic Properties of AgX (X=C, N) in Rock Salt Structure

JAMESON MAIBAM¹, KH. KABITA¹, B. INDRAJIT SHARMA^{1*}, R.K. THAPA² and R.K. BROJEN SINGH³

¹Department of Physics, Assam University, Silchar-788 011 (Assam)

²Physics Department, Mizoram University, Aizawl-796 001 (Mizoram)

³School of Computational and Integrative Sciences, JNU, New Delhi-110 067

*E-mail: indraofficial@rediffmail.com

Abstract

The electronic structure of AgX (X = C and N) is calculated within the framework of density functional theory (DFT) using full potential linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA). The ground state properties for the compounds in rock salt structure are determined. The structural and electronic parameters such as lattice constant, bulk modulus, energy band diagram and density of states are calculated. The energy band diagram and density of states show that both AgC and AgN in rock salt structure possess metallic character and has Fermi energy 0.63 Ry and 0.53 Ry respectively. The energy separation between the lowest band and valence band (E_g^{Ns-Np}), and the band wide ($E_p - E_v$) of valence band of AgN is higher as compared to AgC. The elastic constants C_{11} , C_{12} , C_{44} obtained using volume conserving technique are found to be satisfied for stability conditions: $(C_{11} - C_{12}) > 0$, $(C_{11} + 2C_{12}) > 0$, $C_{11} > 0$, $C_{44} > 0$ and hence AgC, AgN crystallizes in rock salt structure is a stable compound.

Key words : Density functional theory, density of states, elastic constants.

1. Introduction

AgC and AgN are members of the group IB transition metal carbides and nitrides. Based on recent synthesis of noble metals [1-4] and their suggestions of possibility to form nitrides with noble metals such as Au, Ag and Cu, we have chosen to do theoretical investigations on the elastic properties which were not done much earlier. The elastic constants play an important role in the physics of materials as they characterize the behaviour of the crystal in the field of external forces. Paiva et al [5] have performed structural, electronic, and magnetic calculations using the full potential linearized augmented plane wave method (FP-LAPW) on the 4d transition metal nitrides including the AgN in Zinc-blende structure (ZB). They reported that AgN shows a metallic behaviour in the ZB structure. Kanoun et al [4] have performed ab initio (FP-L/APW+LO) calculations on

the structural and electronic properties of AgN and they predicted that the rock salt structure (RS) is the ground state phase of this compound. They calculated charge density in the same work to clarify its bonding character. Fan et al [6] have performed ab initio studies on RuC, PdC, AgC and PtC. They have also calculated the elastic constants C_{ij} , bulk modulus B, shear modulus G, Young's modulus Y and Poisson's ratio of RuC, PdC, AgC and PtC. Engin et al [7] have performed ab initio calculation on hypothetical study of silver nitride.

2. Methods of Calculation

Within the formalism of Density Functional Theory (DFT) [8-10], the total energy is expressed as a functional of density of the electron system, ρ as;

$$E[\rho] = T_o[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho] \quad (1)$$

where, $T_o[\rho]$ is the kinetic energy of a non-interacting electron system, $V_H[\rho]$ and $V_{XC}[\rho]$ are the Hartree and exchange-correlation contributions to the energy and $V_{ext}[\rho]$ is the energy due to the external potential of the system. Thus the corresponding Hamiltonian called the Kohn-Sham Hamiltonian is;

$$\begin{aligned} \hat{H}_{KS} &= \hat{T}_o + \hat{V}_H + \hat{V}_{XC} + \hat{V}_{ext} \\ &= -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{e^2}{4\pi\epsilon_o} \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{XC} + V_{ext} \end{aligned} \quad (2)$$

The exact density of N electron system can be expressed in ground state by, where the single

$$\rho(\vec{r}) = \sum_{i=1}^N \phi_i(\vec{r})^* \phi_i(\vec{r})$$

particle wave functions $\phi_i(r)$ are the N lowest energy solutions of the Kohn-Sham equation: $\hat{H}_{KS} \phi_i = \epsilon_i \phi_i$ of the N electron system. This equation can be solved self-consistently in an iterative process. The calculations of AgC and AgN in rock salt structure are performed with the full potential-linearized augmented plane waves (FP-LAPW) within the framework of the density functional theory (DFT) with generalised gradient approximation (GGA-PBE) for the exchange correlation potential [11]. We have employed the scalar relativistic FP-LAPW method as implemented in the WEIN2k code [12]. 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 divided into non-overlapping atomic spheres whose centre is at atomic position and interstitial region. Inside the muffin tin (MT) region, the potential is a product of radial function and spherical harmonics. For the interstitial region that is outside the muffin tin sphere, the potential are expanded in plane waves. The muffin tin radii (R_{MT}) for silver and non metals are listed in Table I. The convergence of the basis set is controlled by a

cut-off parameter $RMTK_{max} = 9.0$ where K_{max} gives the plane wave cut-off. For every case the wave functions inside the MT spheres which are expanded into spherical harmonics are up to $l = 10$. The number of k points used for the integration procedure is 7000 which reduces to 220 irreducible k points inside the Brillion zone including five high symmetry points W, L, Γ , X and K. The calculations are performed at the equilibrium lattice constants which are determined from a plot of total energy against the unit cell volume by fitting to the Murnaghan equation of state [13].

3. Results and Discussion

3.1 Structural Properties

The unit cell of AgC and AgN in rock salt structure is generated as a first step of the calculation. For the optimization of thus generated structure, total energy of the different sizes of the unit cell is calculated. Figure 1(a, b) shows the total energy curve as a function of volume for AgC and AgN respectively. The total energy verses volume curve is fitted with the Murnaghan equation of state. The structural parameters obtained from the fitting are listed in Table I. In Fig. 1(a), it is observed that the minimum total energy occurs at the volume 166.85 (a.u.³) and thus the equilibrium lattice constant to be 8.739 bohr for AgC. Similarly the equilibrium lattice constant for AgN is found to be 8.699 bohr. It agrees well with the other reported values [4,6,7]. It is noted that disagreements within 6 % are common in first principle calculations based on the density functional theory and are often sensitive to the exchange correlation terms employed.

For cubic systems, there are only three independent elastic constants C_{11} , C_{12} and C_{44} . Hence a set of three equations is needed to determine all the constants, which means that three types of strain must be applied to the starting crystals [14]. The first equation involves calculating bulk modulus (B), which is related to the elastic constants as;

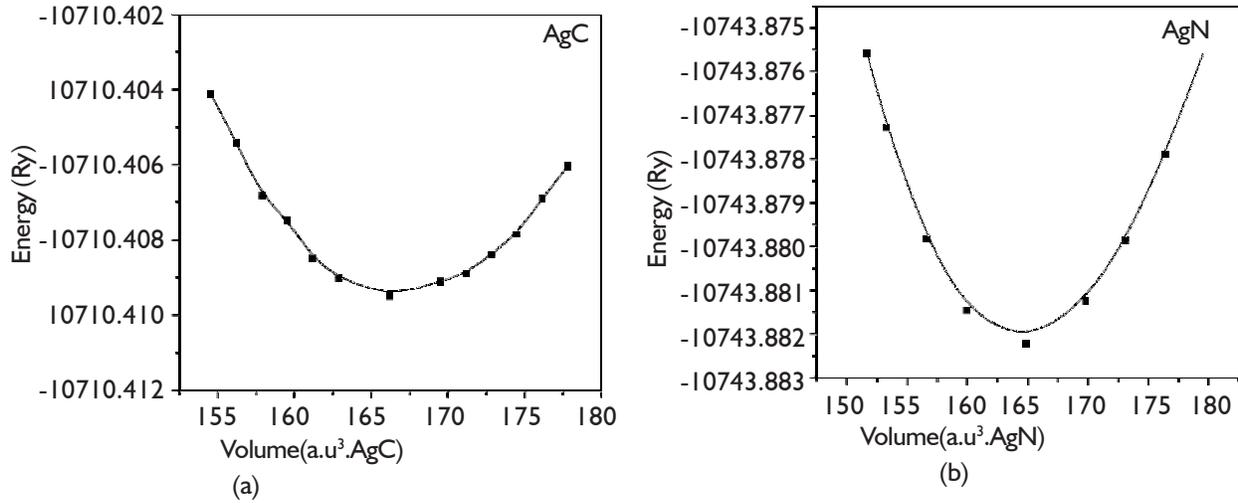


Fig. 1. Total energy vs. volume for (a) AgC and (b) AgN

Table I

Lattice constant ' a_0 ', bulk modulus ' B ', its pressure derivative ' B' ', and muffin-tin radii ' R_{MT} ', density ' ρ ', elastic constants ' C_{11} ', ' C_{12} ' and ' C_{44} ' of AgC and AgN

System	a_0 (bohr)	B (GPa)	B'	R_{MT} (bohr)	ρ (kg/m ³)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
AgC	8.739 8.800 ^a	153.81	5.59	$R_{Ag} = 2.15$ $R_C = 1.95$	4041.15	169.72	151.72	8.89
AgN	8.699 8.409 ^b 8.447 ^c	171.04	3.89	$R_{Ag} = 1.90$ $R_N = 2.05$	4141.58	275.16	103.71	26.68

^aM. B. Kanoun, S. G. Said, Phys. Lett. A. 362 73 (2007); ^bC. Z. Fan, S.Y. Zeng, P. Zhang, Y. G. Yao, App. Phys. Lett. 89 071913 (2006); ^cD. Engin, C. Kemal, C. Y. Oztekin, Chin. Phys. Lett. 25 2154 (2008).

$$B = (1/3)(C_{11} + 2C_{12}) \quad (3)$$

The second one involves performing volume conservative tetragonal strain tensor. Application of this strain has an effect on the total energy from its unstrained value as follows;

$$E(\delta) = E(0) + 3(C_{11}-C_{12})V_o \delta^2 + O(\delta^3) \quad (4)$$

Finally, for the last type of deformation, we use the volume rhombohedral strain tensor. This changes the total energy to

$$E(\delta) = E(0) + (1/6)(C_{11}+2C_{12}+4C_{44})V_o \delta^2 + O(\delta^3) \quad (5)$$

In our calculations, we consider only small lattice distortions in order to remain within the elastic domain of the crystal. Our GGA calculated values of elastic constants C_{11} , C_{12} , C_{44} are given in Table I. As to the best of our knowledge no experimental value for the elastic constant of AgC and AgN in the rock salt structure has been appeared in the literature for comparison and hence the results may be used as a first step for the other theoretical calculations. The mechanical stability conditions on the elastic constants in cubic crystals are known to be $(C_{11}-C_{12}) > 0$, $(C_{11}+2C_{12}) > 0$, $C_{11} > 0$, $C_{44} > 0$ [15]. Our results for the elastic constants in Table I, satisfy these stability conditions, and hence AgC and AgN are mechanically stable.

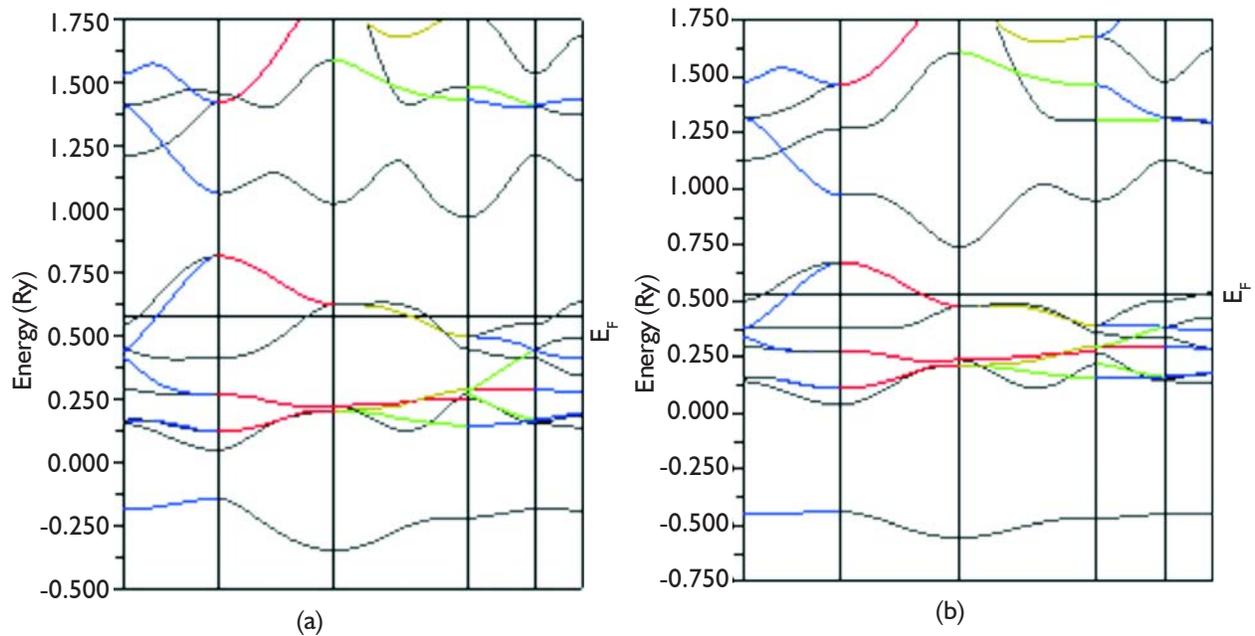


Fig. 2. Energy band diagram of (a) AgC and (b) AgN

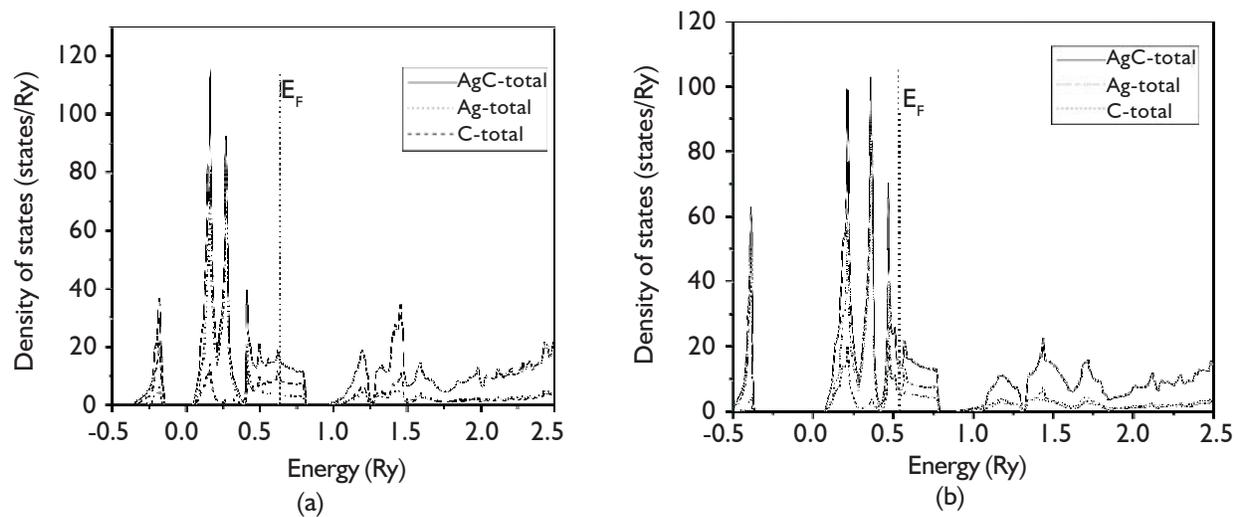


Fig. 3. Total density of states of (a) AgC and (b) AgN

3.2 Bandstructure and Density of States

Figure 2(a, b) shows the energy band diagram of AgC and AgN. In both the energy band diagram, it is observed that the valence band crosses the Fermi level to conduction band and thus predicts both the AgC, AgN in rock salt structure exhibits a metallic nature. This is confirmed as no gap appears at the Fermi level in the total density of states diagrams as shown in Fig. 3(a, b).

Table 2
Characteristic band separations of the band diagram as shown in Fig. 2 (a) and (b)

Energy (Ry)	AgC	AgN
E_F	0.63	0.53
E_g^{Ns-Np}	0.19	0.48
$E_p - E_s$	0.55	0.77

The characteristic band separation (E_g^{Ns-Np}) is the energy separation between the maximum energy of the lowest band (E_{Ns}) and lowest energy of the uppermost band (E_{Np}), ($E_p - E_s$) gives the width of the valence band and are listed in Table 2.

4. Conclusion

In this paper, a systematic FP-LAPW method with GGA have been performed for theoretical study on the electronic structure and elastic properties of AgX (X=C, N) in rock salt structure. The energy band structure clearly shows the valence band (which is mainly contributed from the p band of none metal-C, N and partly d band of Ag) crosses to conduction band at Fermi level. It implies that both the compounds, AgC and AgN exhibits metallic nature and has Fermi energy 0.63 Ry and 0.53 Ry respectively. The energy separation between the lowest band and valence band (E_g^{Ns-Np}), and the band wide ($E_p - E_s$) of valence band of AgN is higher as compared to AgC. The elastic constants C_{11} , C_{12} , C_{44} for both AgC and AgN satisfy the stability conditions: $(C_{11}-C_{12})>0$, $(C_{11}+2C_{12})>0$, $C_{11}>0$, $C_{44}>0$. Thus both AgC, AgN crystallizes in rock salt structure is a stable compound. Although the calculated parameters show interesting results, there is less experimental work. Thus experiments need to be performed to understand the true nature of the compounds.

Acknowledgement

Financial support under the Fast Track Project (SR/FTP/PS-33/ 2006 dt.06.05.2008) from Department of Science and Technology (DST), Government of India is gratefully acknowledged.

References

[1] A. Devia, V. Benavides, H. Castillo and J. Quinterio, *Plasma fusion Sci.*, **258** (2006) 261.

- [2] R. Yua, X.F. Zihang, *Appl. Phys. Lett.*, **86** (2005) 121913.
- [3] J.H. Quinterio, R. Ospina, O.O. Cardenas, G. I. Alzate and A. Devia, *Phys. Scr.*, **T131** (2008) 014013.
- [4] M.B. Kanoun and S.G. Said, *Phys. Lett.*, **A 362** (2007) 73.
- [5] R. De Paiva, R.A. Nogueira and J.L.A. Alves, *Brazilian Journal of Physics*, **36** (2006).
- [6] C.Z. Fan, S.Y. Zeng, P. Zhang and Y.G. Yao, *App. Phys. Lett.*, **89** (2006) 071913.
- [7] D. Engin, C. Kemal and C.Y. Oztekin, *Chin. Phys. Lett.*, **25** (2008) 2154.
- [8] S. Cottenier, Density Functional Theory and the family of (L) APW-methods: a step-by-step introduction (Belgium, Insti-tuut voor Kern-en Stralingsfysica, K.U.Leuven ISBN 90-807215-1-4) (2002).
- [9] P. Hohenberg and W. Kohn, *Phys. Rev.*, **136** (1964) 864.
- [10] W. Kohn and L.J. Sham, *Phys. Rev.*, **140**(1965) 1133.
- [11] J.P. Perdew, S. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, **77** (1996) 3865.
- [12] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka and J. Luitz, WIEN2k An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties (Austria, Karlheinz Schwarz, Techn. Universitat Wien, ISBN3- 9501031-1-2) (2001).
- [13] F.D. Murnaghan, *Proc. USA Natl. Acad. Sci.*, **30** (1944) 244.
- [14] E. Schreiber, O.L. Anderson and N. Soga, Elastic Constants and Their Measurements, (McGraw- Hill, New York) (1973).
- [15] M. Born, K. Huang, Dynamical Theory of Crystal Lattices (Claredndon, Oxford) (1956).