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The energy band gap of ScN in the rocksalt phase obtained with LDA/GGA+U^{SIC} approximations in FP-LAPW method

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ABSTRACT

The structural properties of scandium nitride compound (ScN) in the rocksalt phase (RS) have been calculated using the full potential linearized augmented plane wave (FP-LAPW) method within the local density (LDA), Predew–Burke–Ernzerhof (PBE-GGA), Wu–Cohen (WC-GGA), and Engel–Vosko (EV-GGA) approximations. The influence of electron correlation has also been considered in calculating the electronic structure of RS–ScN within the LDA+U^{SIC}, PBE-GGA+U^{SIC}, WC-GGA+U^{SIC}, and EV-GGA+U^{SIC} approximations. For the system of interest, the calculations show that EV-GGA and PBE-GGA approximations give more accurate values for the lattice parameter (a_0) and bulk modulus (B_0) than LDA and WC-GGA approximations. The calculations also show that EV-GGA+U^{SIC} approach improves the description of the electron structure of RS–ScN than LDA+U^{SIC}, WC-GGA+U^{SIC} and PBE-GGA+U^{SIC} methods. The energy band gap of RS–ScN within EV-GGA+U^{SIC} scheme is found to be 1.09 eV. This value is in excellent agreement with the experimental value of about 0.8–1.6 eV.

1. Introduction

The well-known IIIA-N (such as GaN, InN, AlN, and their alloys) were extensively studied both experimentally and theoretically due to their important in electronic and optoelectronic devices. On the other hand, IIIB-N (such as ScN, YN, and LaN) have been less studied in spite of their importance technological applications. In particular, ScN has very interesting physical properties. It has a high melting point (~2600 °C), hardness and mechanical strength. Its high melting point makes ScN suitable for high temperature ohmic contacts for IIIA-N [1].

ScN was investigated by Scalar [2]. He made electrical and optical measurements on pressed-powder samples of ScN. He found that ScN has metallic behaviour. In contrast, his optical transmission measurements on evaporated films of ScN predicted a semiconductor behaviour with an energy gap of 2.6 eV. Travaglini et al. prepared ScN samples and made optical reflecting measurements in photon energy range between 12 eV down to 1 meV at room temperature [3]. They also measured their electrical resistivity by four prob method and Hall effect at room temperature. They concluded that ScN has metallic character. Zheng et al. reported the crystal growth of ScN on a tungsten foils by sublimation–recondensation method in the temperature range of 1840–2060 C°, pressure range of 15–230 Torr under nitrogen atmosphere [4]. They found that the crystal structure is rocksalt with lattice constant 4.5005 A°. On the other hand, Bai and Kordesch prepared ScN samples by two methods, plasma assisted physical vapour deposition (PAPVD) and reactive rf-sputtering [1]. The average lattice constant obtained was 4.4717 A°, and optical band gap values 2.73–3.2 eV, for films prepared by PAPVD and 2.26–2.77 eV for films by sputtering. Niewa et al. prepared ScN samples, and they reported a rocksalt crystal structure (RS) with lattice constant 4.512 A° [5]. Gall et al. studied the electronic structure of ScN by optical spectroscopy, photoemission and preformed an ab initio Khon–Sham approach, which treats the exchange interaction exactly with density functional theory [6]. From their experimental and calculation investigations, they concluded that ScN is a semiconductor with an indirect Γ–X band gap of 1.3 ± 0.3 eV and direct band gap at Γ of 2.4 ± 0.3 eV [6]. ScN thin films have been prepared using chemical vapour deposition [7], molecular beam epitaxy [9,10], magnetron sputtering [8]. Recently, Moram et al. reported the growth of ScN thin films on silicon substrates by molecular beam epitaxy at low relative temperature (~850 C°) [11].

Various computational methods have also been used in calculating the electronic structure of ScN. Lambrecht used linear muffin-tin orbitals (LMTO) method in the atomic sphere approximation (ASA) in studying the electronic structure of ScN and GdN [12]. He found that ScN is a semiconductor with indirect gap Γ–X of 0.9 eV, direct gap at X of 2.0 eV and direct gap at Γ of 4.3 eV. Later on Takeuchi [13] used full potential linearized augmented plane wave (FP-LAPW) method as implemented in WIEN97 code

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[14]. He obtained good structural parameters, but zero-energy gap. Using screened exchange (SX) LDA approach, Stampfl et al. calculated the electronic structure for ScN, YN and LaN [15]. They found that all of these materials are indirect semiconductors of energy gaps 1.58, 0.85, and 0.75 eV, respectively. Recently, Qteish et al. used exact based quasiparticle energy calculations (KS-DFT) within an ab initio pseudopotential in calculating the electronic structure of ScN [16]. They obtained energy gap of 0.9 ± 0.1 eV. On April 2007, Tran et al. have reported GGA calculations with the Engel–Vosko functional for semiconductors and insulators [17]. They found that ScN is a semiconductor with energy gap of 0.2 eV.

As seen above there are some contradictions in the published reports about the band gap energy of RS–ScN. Some reports claim that RS–ScN is a semiconductor with a small energy gap between N 2*p* valance band and Sc 3*d* conduction band [3,17–19], while others claim that RS–ScN is a semiconductor of indirect energy band gap with band gap energy of 0.8–1.6 eV [4,6,7,12,16]. In contrast, some reports claim that Rs–ScN is a semimetal [20–22].

Since many physical properties depend on the band gap energy, the aim of this study is to cure the energy band gap of RS–ScN compound using LDA, PBE-GGA, WC-GGA, and EV-GGA approaches plus an appropriate value of an on site Coulomb self-interaction-like correction potential (U^{SIC}). Adding an appropriate value of (U^{SIC}) leads to a discontinuity in the exchange-correction potential and thus improves the band gap energies of semiconductors, especially the strongly correlated *d* or *f* semiconductors [23–26]. In the present paper, we have also examine the structural properties of RS–ScN using FP-LAPW method within LDA, PBE-GGA, WC-GGA, and EV-GGA approximations.

After a description of the computational details, we present and discuss the structural and electronic properties of the RS–ScN material. The conclusion is given in Section 4.

2. Computational details

The calculations were performed using FP-LAPW method as implemented in the WIEN2K code [27] within the framework of density functional theory (DFT) [28]. The structural and electronic properties of ScN in the RS phase were calculated using LDA [29,30], PBE-GGA [31,32], WC-GGA [33], and EV-GGA [34] approximations.

In order to get a better value of the band gap energy for RS–ScN phase, we have applied LDA, PBE-GGA, WC-GGA, and EV-GGA plus an on-site Coulomb self-interaction correction potential (U). Threre are two versions of the LDA+U method, LDA+U^{SIC} [35,37] and LDA+U^{AMF} [38]. LDA+U^{SIC} method is suitable for strongly correlated systems such as ScN, while LDA+U^{AMF} is suitable for less strongly correlated systems. So, in this paper LDA+U^{SIC}, PBE-GGA+U^{SIC}, WC-GGA+U^{SIC}, and EV-GGA+U^{SIC} approximations were used to calculate the band structure of the RS-ScN phase. The LDA+U^{SIC}, PBE-GGA+U^{SIC}, WC-GGA+U^{SIC}, and EV-GGA+U^{SIC} methods were used with the "SIC" double-counting scheme of Anisimov et al. [37], which is appropriate for strongly *d* or *f* correlated electrons as mentioned earlier.

In the LDA+U^{SIC}, PBE-GGA+U^{SIC}, WC-GGA+U^{SIC}, and EV-GGA+U^{SIC} methods, the strong correlation between localized *d*-electrons is explicitly taken into account through the screened effective electron-electron interaction parameter $U_{eff} = U^{SIC} - J$, where U^{SIC} and *J* denote the coulomb and exchange integrals, respectively [35–37]. To obtain the best agreement with experiment, the present results were obtained with $U^{SIC} = 6$ eV and $J = 0$ (i.e., $U_{eff} = 6$ eV). The value of the U^{SIC} correction (i.e., 6 eV) was determined by optimizing the band gap energy to the experimental value. This means that we have increased the value of U^{SIC} until we get a very closed energy band gap to the experimental value. However, it was found that changing U^{SIC} does not affect the values of the lattice constant and bulk modulus.

It is worth noting that we have done the band structure the calculations using LSDA approximation (local spin density approximation), but we found that the band gap energy would not be changed and the magnetic moment per unit cell was found to be zero. Therefore, LSDA calculations are not needed here. On the other hand, this paper does not include the calculations of the effective mass; so that spin orbit coupling is also not needed here.

The Sc 3*d* electrons were treated as valence. Inside the atomic spheres, the partial waves were expanded up to $l_{max} = 10$. Whereas, in the interstitial region they are expanded in terms of plane waves (PWs). The number of plane waves cut-off was limited by $R_{MT}K_{max} = 8.0$ for LDA and LDA+U^{SIC}, and $R_{MT}K_{max} = 9.0$ for PBE-GGA, PBE-GGA+U^{SIC}, WC-GGA, WC-GGA+U^{SIC}, EV-GGA, and EV-GGA+U^{SIC} calculations, where K_{max} is the maximal value of the reciprocal lattice vector used in the plane wave expansion, and R_{MT} is the smallest muffin-tin radius in the unit cell. In the unit cell, the atomic spheres radii were chosen in such a way that they are just touching. With this choice for R_{MT}, the spheres of Sc and N are sufficiently large so that the leakage of the d electrons outside the spheres is very small. The muffin-tin radii R_{MT} were chosen as 2.02 bohr, and 1.79 bohr for Sc and N, respectively.

The charge density was Fourier-expanded with $G_{max} = 14Ry^{1/2}$ for LDA and LDA+U^{SIC}, and $G_{max} = 16Ry^{1/2}$ for PBE-GGA, WC-GGA, EV-GGA, PBE-GGA+U^{SIC}, WC-GGA+U^{SIC}, and EV-GGA+U^{SIC}.

A *K*-mesh of 3000 *K*-points in the full Brillouin zone or 104 *K*-points in the irreducible Brillouin zone (IBZ) was used. A sufficiently dense *K*-point grid was used to achieve a convergence of the total energy to better than 0.1 mRy, namely a regular $14 \times 14 \times 14$ Monkhorst–Pack (MP) mesh for the RS phase [39].

3. Results and discussion

3.1. Structural properties

The lattice constant a_0, bulk modulus B_0 and its pressure derivative B_0' were calculated from the Murnaghan's equation of state [40] using LDA, PBE-GGA, WC-GGA, and EV-GGA approximations. We first determine the equilibrium volume of the ground state of the RS phase of ScN compound by calculating the total energy per primitive unit cell as a function of the volume. The Murnaghan's equation of state is then used to fit the calculated energy-volume data.

The structural parameters a_0, B_0, and B_0' are listed in Table 1. The results of other ab initio calculations and experimental values are also listed in Table 1. The data shown in Table 1 indicate that LDA underestimates a_0 by 1.56%, PBE-GGA overestimates a_0 by 0.39%, WC-GGA underestimates a_0 by 0.63% and EV-GGA overestimates a_0 by 0.29%. GGAs calculations, therefore, improve a_0 significantly over LDA. The data listed in Table 1 also show that the GGAs calculations produce more accurate bulk modulus than LDA. This clearly demonstrates that the GGAs approaches are associated with some correlation effects beyond LDA scheme.

3.2. Electronic properties

The calculated relativistic electronic band structures of ScN in the RS phase at ambient pressure along principal high symmetry points in the Brillouin zone using LDA, LDA+U^{SIC}, WC-GGA, WC-GGA+U^{SIC}, PBE-GGA, PBE-GGA+U^{SIC}, EV-GGA, and EV-GGA+U^{SIC} are displaced in Figs. 1–4, respectively. The band structures have been calculated at the experimental lattice constant $a_0 = 4.501$ A°. The zero-energy reference is the valence-band maximum. It occurs

Table 1
Calculated lattice constant a_0, bulk modulus B_0 and its first derivative B_0' of ScN in RS phase.

Present calculations				Experiment	Other calculations
LDA	PBE-GGA	WC-GGA	EV-GGA	Ref. [7]	–
a_0 (A°) 4.431	4.518	4.473	4.514	4.501	4.455[a], 4.533[b]
B_0 (GPa) 222	193	207	194	182 ± 40	221[a], 196[b]
B_0' 4.24	4.01	4.14	4.06	–	4.27[a], 4.36[b]

[a] PP-PW (LDA).
[b] PP-PW (GGA) Ref. [16].

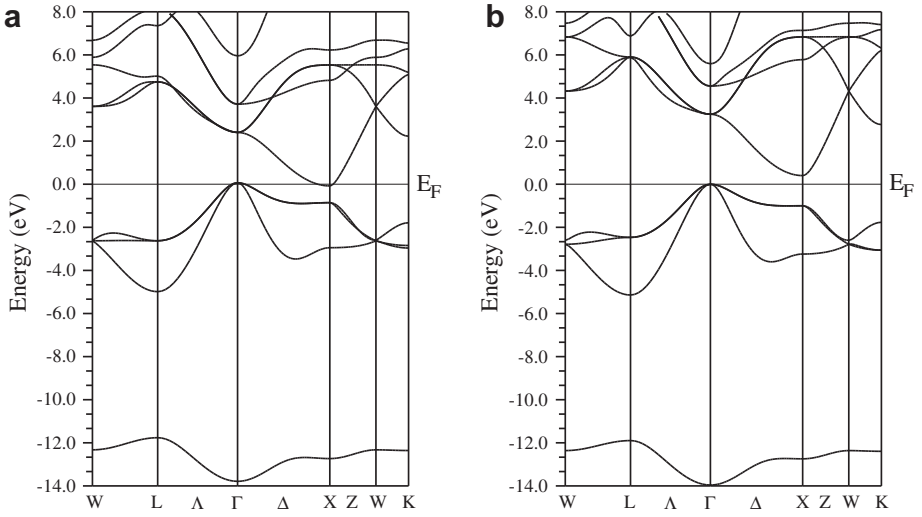

Fig. 1. Energy band structure of RS–ScN using (a) LDA and (b) LDA+U^{SIC} methods.

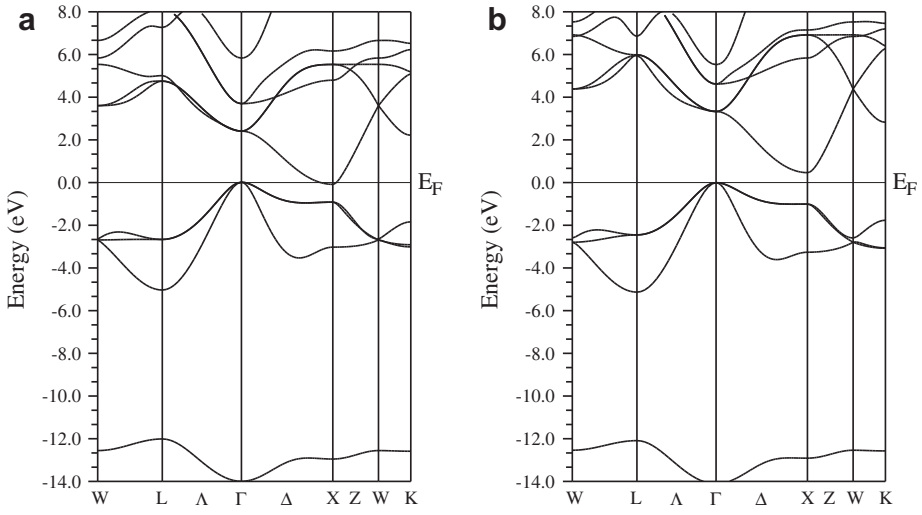

Fig. 2. Energy band structure of RS–ScN using (a) WC-GGA and (b) WC-GGA+U^{SIC} methods.

at the Γ-point. The conduction band minimum occurs at the X-point. The energy band gap of RS–ScN is Γ–X indirect band gap.

In Figs. 1a, 2a, 3a, and 4b, the LDA, PBE-GGA , WC-GGA, and EV-GGA approximations have been shown to give indirect band gap energies of −0.15 eV, −0.03 eV, −0.10 eV, and 0.46 eV, respectively, between the valence-band maximum (at Γ-point) and the conduction band minimum (at the X-point). These calculated gaps are listed in Table 2. In LDA, PBE-GGA, and WC-GGA calculations RS-ScN is a metallic like compound, while in EV-GGA calculation it is a semiconductor. Despite the many successes of the LDA, PBE-GGA, and WC-GGA approximations, they are still insufficient for studying the electronic structure of strong correlated materials such as ScN. They show ScN to be metal, while in reality it is a semiconductor with a measured band gap energy of about 0.8–1.6 eV [6,7]. The improved energy band gap obtained by EV-GGA method, however, makes it more suitable for treatment of the systems with strong electron correlation. Although EV-GGA approach has been shown to give band gap energy for RS–ScN in better

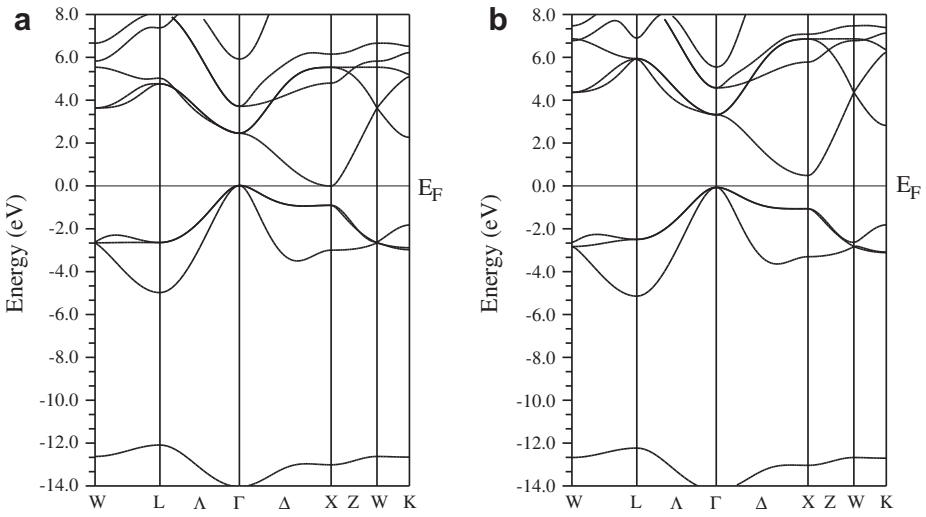

Fig. 3. Energy band structure of RS–ScN using (a) PBE-GGA and (b) PBE-GGA+U^{SIC} methods.

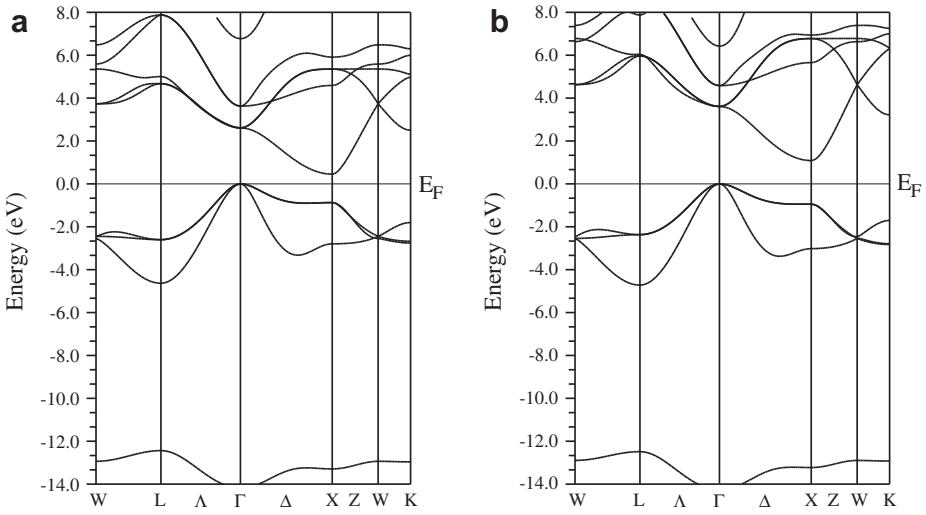

Fig. 4. Energy band structure of RS–ScN using (a) EV-GGA and (b) EV-GGA+U^{SIC} methods.

Table 2
Calculated and experimental energy band gap (E_g) of RS–ScN (in eV).

Approach	$E_g^{\Gamma-X}$	E_g^{X-X}	$E_g^{\Gamma-\Gamma}$
Present calculations			
LDA	−0.15	0.78	2.34
PBE-GGA	−0.03	0.90	2.44
WC-GGA	−0.10	0.83	2.40
EV-GGA	0.46	1.33	2.61
LDA+U^{SIC}	0.40	1.40	3.25
WC-GGA+U^{SIC}	0.47	1.47	3.34
PBE-GGA+U^{SIC}	0.55	1.55	3.39
EV-GGA+U^{SIC}	1.09	2.03	3.61
Other theoretical calculations Ref. [16]			
LDA-G_oW_o	1.14	2.06	3.71
OEPX (CLDA)	0.84	1.98	3.51
$(G_oW_o)_{average}$	0.99	2.02	3.62
PP-PW (GGA)	−0.03	0.87	2.43
PP-PW (LDA)	−0.15	0.75	2.34
Experiment			
–	1.3 ± 0.3[a]	2.4[a]	3.8[a]
–	0.9 ± 0.1[b]	2.15[b]	–

[a] Ref. [6].
[b] Ref. [7].

agreement with experimental than LDA, PBE-GGA, and WC-GGA approaches, its improvement is small for highly correlated systems such as ScN.

In order to solve the band gap problem for RS–ScN, we have applied LDA, PBE-GGA, WC-GGA, and EV-GGA plus an on-site Coulomb self-interaction correction potential (U^{SIC}). As mentioned before, a U^{SIC} of 6 eV is used. In Figs. 1b, 2b, 3b, and 4b the LDA+U-^{SIC}, WC-GGA+U^{SIC}, PBE-GGA+U^{SIC}, and EV-GGA+U^{SIC} have been shown to give band gap energies of 0.4 eV, 0.47 eV, 0.55 eV, and 1.09 eV, respectively. These calculated gaps are also listed in Table 2. The self-interaction correction potential (U*SIC*), therefore, opens the band gap of Rs–ScN and hence yields a semiconductor behaviour. Similar to the EV-GGA method, the gap obtained by LDA+U^{SIC}, WC-GGA+U^{SIC} and PBE-GGA+U^{SIC} approaches is smaller than the experimental gap, whereas the EV-GGA+U^{SIC} approximation produces the correct band gap energy (0.8–1.6 eV). It is clearly seen that the band gap energy of RS–ScN is strongly improved using EV-GGA+U^{SIC} approach when the suitable value of the U^{SIC} is considered. Therefore, we get an excellent result compared to other theoretical calculations, like pseudopotential calculations [16], and to experimental value [6,7] when U^{SIC} is considered to be

6 eV. It seems that the EV-GGA+U^{SIC} is more efficient method for treatment the compounds involving *d*-orbitals such as ScN.

4. Conclusion

In the present work we propose the structural and electronic properties of ScN in the RS phase using LDA, PBE-GGA, WC-GGA, and EV-GGA approaches as implemented in the WIEN2K program. The lattice constant and bulk modulus produced by the GGAs approaches are found to be in a very good agreement with the available experimental results, while the band gap energy produced by LDA, PBE-GGA, and WC-GGA approaches is far from the measured value. While RS–ScN is found to be semimetallic compound (an almost zero indirect band gap) in LDA, PBE-GGA, and WC-GGA calculations, it is a semiconductor compound (with small indirect band gap energy) in the EV-GGA calculation.

To obtain the best agreement with experiment, we have also reported the band gap energy of ScN in the RS phase using the LDA+U^{SIC}, PBE-GGA+U^{SIC}, WC-GGA+U^{SIC}, and EV-GGA+U^{SIC} approximations as implemented in the WIEN2K program. Similar to EV-GGA calculation, the band gap energy obtained by LDA+U^{SIC}, PBE-GGA+U^{SIC}, and WC-GGA+U^{SIC} is smaller than the experimental value. In contrast, EV-GGA+U^{SIC} approach yields a gap of 1.09 eV, which is very consistent with the experimental results as well as with the other theoretical calculations, like pseudopotential calculations. This indicates that EV-GGA+U^{SIC} is an efficient method for calculating the energy band gap of ScN compound in the rocksalt phase.

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References

[1] X. Bai, M.E. Kordesch, Appl. Surf. Sci. 175–176 (2001) 499.
[2] N. Scalar, J. Appl. Phys. 35 (1964) 1534.
[3] G. Travaglini, F. Marabelli, R. Monnier, E. Kaldis, P. Wachter, Phys. Rev. B 34 (1986) 3876.
[4] Z. Gu, J.H. Edgar, J. Pomeroy, M. Kuball, D.W. Coffey, J. Mater. Sci.: Mater. Electron. 15 (2004) 555.
[5] R. Niewa, D.A. Zherebtsov, M. Kirchner, M. Schmidt, W. Schnelle, Chem. Mater. 16 (2004) 5445.
[6] D. Gall et al., Phys. Rev. B 63 (2001) 125119.
[7] H. Al-Brithen, H. Yang, A.R. Smith, J. Appl. Phys. 96 (2004) 3787.
[8] D. Gall, I. Petrov, L.D. Madsen, J.E. Sundgren, J.E. Green, Vac. Sci. Technol. A 16 2411 (1998).
[9] H. Al-Brithen, A.R. Smith, Appl. Phys. Lett. 77 (2000) 2485.
[10] H. Al-Brithen, E.M. Trifan, D.C. Ingram, A.R. Smith, D. Gall, J. Cryst. Growth 242 (2002) 345.
[11] M.A. Moram, T.b. Joyce, P.R. Chalker, Z.H. Barber, C.J. Humphreys, Appl. Surf. Sci. 252 (2006) 8385.
[12] W.R.L. Lambrecht, Phys. Rev. B 62 (2000) 13538.
[13] N. Takeuchi, Phys. Rev. B 65 (2002) 045204.
[14] P. Blaha, K. Schwarz, J. Luitz, Wien97 (1999).
[15] C. Stampfl, W. Mannstadt, R. Asahi, A.J. Freeman, Phys. Rev. B 63 (2001) 155106.
[16] A. Qteish, P. Rinke, M. Scheffler, J. Neugebauer, Phys. Rev. B 74 (2006) 245208.
[17] F. Tran, P. Blaha, K. Schwarz, J. Phys. Condens. Matter 19 (2007) 196208.
[18] A. Neckel, P. Rastel, R. Eibler, P. Weinberger, K. Schwarz, J. Phys. C 9 (1976) 579.
[19] R. Monnier, J. Rhyner, T.M. Rice, D.D. Koelling, Phys. Rev. B 31 (1985) 5554.
[20] A. Maachou, B. Amrani, M. Driz, Physica B 388 (2007) 384.
[21] S. Duman, S. Bağci, H.M. Tutuncu, G. Uğur, G.P. Srivastava, Diam. Realted Mater. 15 (2006) 1175.
[22] L. Tie-Yu, H. Mei-Chun, P. Desjardins, Chinese Phys. 16 (2006) 62.
[23] P. Novak, F. Boucher, P. Gressier, P. Blaha, K. Schwarz, Phys. Rev. B 63 (2001) 235114.
[24] I.V. Solovyev et al., Phys. Rev. B 50 (1994) 16861.
[25] C. Person, S. Mirbt, Brazilian J. Phys. 36 (2006) 286.
[26] C. Person et al., Microelectron. J. 37 (2006) 686.
[27] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2K, in: K. Scharz (Ed.), An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Vienna University of Technology, Austria, 2001. (ISBN:3-9501031-1-2).
[28] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.
[29] J. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
[30] P.A.M. Dirac, Proc. Camb. Philos. Soc. 26 (1930) 376.
[31] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[32] J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) 1396.
[33] Z. Wu, R.E. Cohen, Phys. Rev. B 73 (2006) 235116.
[34] E. Engel, S.H. Vosko, Phys. Rev. B 47 (1993) 13164.
[35] I.I. Mazin, V.I. Anisimov, Phys. Rev. B 55 (1997) 12822.
[36] V.I. Anisimov, J. Zaanen, O.K. Anderson, Phys. Rev. B 44 (1991) 943.
[37] V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyzyk, G.A. Sawatzky, Phys. Rev. B 48 (1993) 16929.
[38] M.T. Czyzyk, G.A. Sawatsky, Phys. Rev. B 49 (1994) 14211.
[39] H.J. Monkhorst, L.D. Pack, Phys. Rev. B 13 (1976) 5188.
[40] F.D. Murnaghan, Proc. Natl. Acad. Sci. (USA) 30 (1944) 5390.