Vol 16 No 1, January 2007
1009-1963/2007/16(01)/0062-05

Chinese Physics

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Electronic structure of ScN and YN: density-functional theory LDA and GW approximation calculations*

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(Received 14 March 2006; revised manuscript received 6 June 2006)

The desirable physical properties of hardness, high temperature stability, and conductivity make the early transition metal nitrides important materials for various technological applications. To learn more about the nature of these materials, the local-density approximation(LDA) and GW approximation i.e. combination of the Green function G and the screened Coulomb interaction W, have been performed. This paper investigates the bulk electronic and physical properties of early transition metal mononitrides, ScN and YN in the rocksalt structure. In this paper, the semicore electrons are regarded as valance electrons. ScN appears to be a semimetal, and YN is semiconductor with band gap of 0.142 eV within the LDA, but are in fact semiconductors with indirect band gaps of 1.244 and 0.544 eV respectively, as revealed by calculations performed using GW approximation.

Keywords: ScN ,YN, GW approximation, LDA

PACC: 3150, 7115A

1. Introduction

The early transition-metal mononitrides crystallize in the rocksalt structure and exhibit extreme and unique physical properties of hardness, brittleness, high melting point, and in some cases, superconductivity. They have technological applications in the area of, for example, hard coatings for cutting tools[1] and possible potential for applications in magnetic recording and sensing.[2,3] These materials are metallic, with the exception of ScN (and possibly YN), for which there have been conflicting reports in the literature. Early experiments indicated that ScN is an indirect semimetal,[4] as supported by density-functional theory (DFT) calculations performed within the local-density approximation (LDA).[5] More recent experiments, however, report that it is a semiconductor,[6−9] confirming recent theoretical investigations. In Stampfl *et al*'s work using the screened-exchange (SX)-LDA approach[10] he reported that ScN and YN are indirect semiconductors, with gaps of 1.58 eV and 0.85 eV respectively, whereas within the LDA they are all semimetals. Also two other very recent calculations of the band structure of ScN have been performed, one which includes quasiparticle corrections[11] and the other employing the exact exchange formalism;[8] both of them also find that it is an indirect semiconductor, the reported band gaps are 0.9 and 1.6 eV respectively. In Ref.[11] it was also concluded that GdN is a narrow band-gap semiconductor with a gap of 0.7–0.85 eV. Except ScN, there are not availably experimental data of these early transition-metal (refractory) nitrides. And the theoretical band gap of ScN has a large range (0.9–1.6 eV). Therefore, the generic electronic properties should still be the focus.

Since the Kohn–Sham eigenvalues in the DFT are actually Lagrange parameters in minimizing the total energy, these are not the quasiparticle energies by construction. It is well known that the LDA band gaps are consistently smaller than the experimental values by about 0.5–5.0 eV in semiconductors and insulators. For Ge, the LDA gives a semimetal rather than an indirect gap semiconductor.[12] Even the eigenvalues using the exact exchange–correlation functional within the Kohn–Sham formalism cannot reproduce the exact band gap due to the discontinuity in the potential's functional derivative.[13] In order to get rid of the shortcoming of LDA, several effective methods can be used, such as gradient corrections, LDA+U, self-interaction correction, screened-exchange LDA, exact-exchange LDA and GW approximation, i.e. combination of the Green function G and the screened

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Coulomb interaction W. In this paper, we use LDA and GW approximation to study the electronic structures of ScN and YN. In the calculations, the semicore electrons of Sc and Y are regarded as valence electrons. The results of our work show that ScN and YN are semiconductors with band gap 1.244 eV and 0.544 eV respectively.

This paper is organized as follows. In Section 2 we briefly address the theoretical framework of GW approximation. In Section 3 we present our band structure results for the compound semiconductors ScN and YN and discuss the physical properties of these materials. A short summary concludes the paper in Section 4.

2. Theoretical framework

Our computational approach was presented in detail in Ref.[13]. Here we only summarize a few formal aspects which are particularly important for the systems addressed in this work.

The GW approximation method is usually based on the results of preceding LDA calculations that have to be performed at first. All the *ab initio* pseudopotentials used here were generated with the Troullier–Martin method[14] and the Ceperley–Alder correlation functional.[15] From these calculations, we obtain the LDA wavefunctions and LDA band structure energies.

Using these LDA results, we construct the GW self-energy operator, $\Sigma = \mathrm{iGW}$, where G is the LDA Green function and W is the screened Coulomb interaction.[16,17] In the evaluation of W we employ the random-phase approximation[16,17] and a plasmon-pole mode[18] to include the dynamics of the screening. The difference between the self-energy operator and the LDA exchange–correlation (XC) potential constitutes a perturbation operator. Evaluating its contribution to first order we have the quasiparticle band structure

$$E^{\mathrm{qp}}_{n,k} = \varepsilon^{\mathrm{LDA}}_{n,k} + < n,k| \sum - V^{\mathrm{LDA}}_{xc} |n,k > . \qquad (1)$$

The self-energy operator and a number of other functions entering Σ are spatial two-point functions depending on (r, r').

The use of appropriate potentials is a crucial point in any pseudopotential approach. If the overlap between the core and valence charge densities is not negligible, their contributions to the XC energies cannot be simply separated, and make it difficult to partition electrons. One approach to design a good pseudopotential is to use a partial-core correction[19] that carries over a partial charge of core electrons in the evaluation of exchange and correlation for solids. This usually results in better structural properties. Alternatively, one may attempt to include some of the core states in the pseudopotential as this is particularly important for materials with shallow core states. For example, shifting states from the core into the valence for some II–VI semiconductors has yielded quasiparticle energies in good agreement with the experiment.

In this paper, we have examined the latter option. It has been recognized that for Sc the wave function of the outer core states (3s and 3p) has a substantial overlap with that of the valence states (4s and 3d). A similar situation occurs in Y. In order to obtain good structural properties within the LDA, one needs to include these semicore states explicitly in pseudopotential calculations. Since quasiparticle calculations require an accurate description of screening, a careful examination of the effect due to the semicore states is needed. In general, the exchange and correlation effects between the core and valence electrons are nonlocal and energy dependent. The effective interaction between the valence electrons is modified by the interaction of core dipoles with the fluctuating valence charge. For the anion N of the compounds we employ conventional N^{+5} pseudopotential throughout this paper, i.e. its semicore states are treated as core states. This is reasonable since the anionic semicore states are much lower in energy than the cationic semicore states. The influence of the anionic semicore states on the band structures is therefore very small. So the electronic configurations of the Sc and Y atoms are $(\mathrm{Ne})3s^2 3p^6 3d^1 4s^2$ and $(\mathrm{Ar})4s^2 4p^6 4d^1 5s^2$ respectively. We obtain Sc^{+11} and Y^{+11} pseudopotentials. In the following sections we discuss our results for the studied solids.

3. Results and discussion

The appropriate cutoff used here is needed to obtain converged eigenfunctions and eigenvalues which are used as input for the quasiparticle calculations. No significant change is seen in our work by increasing the cutoff further to 80 Ry. Meanwhile, 19 special K points corresponding to $5 \times 5 \times 5$ with shifted 0.5 Monkhorst–Park mesh are used for the Brillouin zone

integration. Table 1 gives the lattice constants at rocksalt structure for ScN and YN used in our calculation.

Table 1. The lattice constants and band gaps.

	a_0/arb. units		E_g/eV		
	LDA	Expt	LDA	GW	Expt
ScN	8.861	8.503	−0.108	1.244	1.3±0.3
YN	9.363	9.216	0.142	0.544	

In this section we present our theoretical quasiparticle energies for the compounds, together with available experimental results.

The band structures for ScN and YN in the rocksalt phase are given in Figs.1 and 2 respectively. The LDA result of ScN show that ScN is a semimetal material. This agrees with previous theoretical calculations.[10] But the LDA band structure of YN shows that YN is an indirect gap semiconductor, though the band gap is only 0.142 eV.

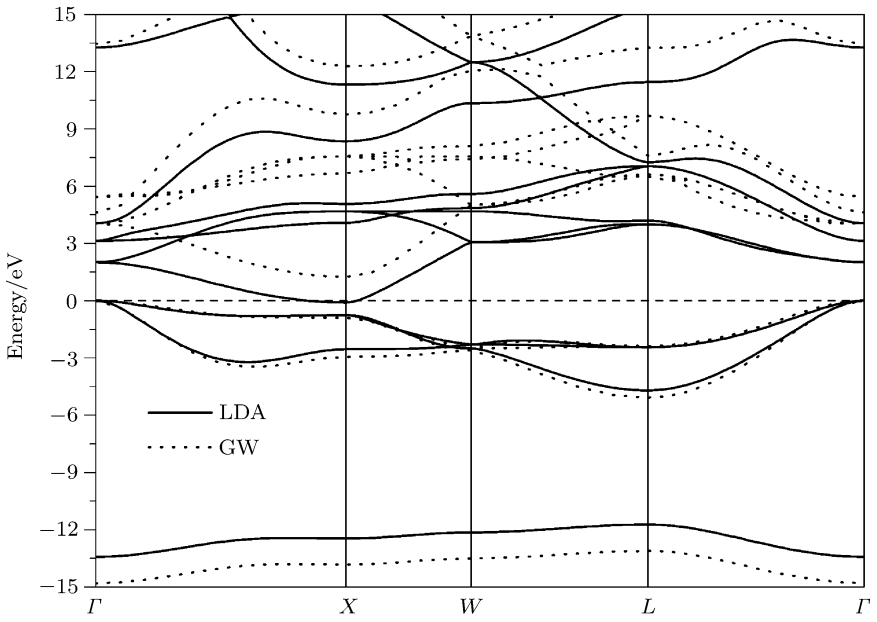


Fig.1. ScN band structure.

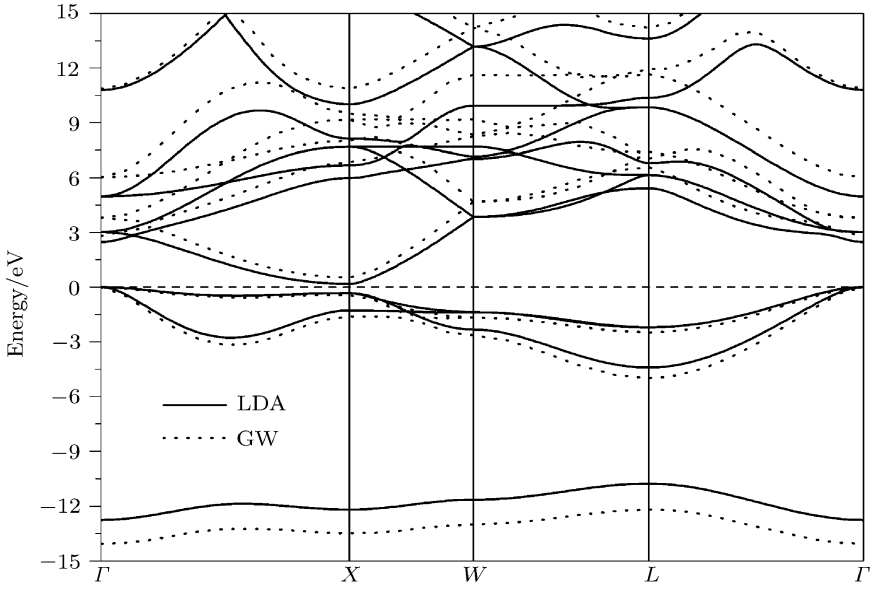


Fig.2. YN band structure.

This is contradictive to the result of Stampfl *et al.*[10] Comparing with the result of Stampfl *et al*, we find that YN's shape of valence and conduction bands are similar. But the valence and conduction bands move along oppositely directions. We have analysed the differences between our results and Stampfl *et al*'s ones. The semicore electrons are regarded as valence electrons in our calculations, meanwhile Stampfl *et al* regarded the semicore electrons as core electrons. Along with increase of valence electrons, the repulsive interaction increase between the valence electrons, and the conduction bands move up obviously. So we find that YN is an indirect gap semiconductor. This illuminates that in LDA the semicore states should be still carefully treated, especially overlap of valance and conductor bands is very little as YN.

The eigenvalues from the LDA and GW calculations for ScN and YN in rocksalt structure are listed in Tables 2 and 3 for four high symmetry points in Brillouin zone. All energies are in reference to the top of the valence band (Γ_8^v). The calculated minimum band gaps of GW approximation are found to be 1.244 eV and 0.544 eV for ScN and YN respectively. The top of valance bands is at Γ, and the bottom of conduction bands is at X for the compounds. The result is in good accord with existing experimental data of 1.3 ± 0.3 eV for ScN.[8] Although there is no availably experimental gap value for YN, our result accords with the SX-LDA result.[10] Figures 1 and 2 show that the upper valence bands of GW agree with the ones of LDA, but the conduction bands move up obviously. So the GW calculations open the gaps. Meanwhile, with respect to the corresponding LDA calculations, both the valence and conduction bandwidths broaden. Because of the nonlocal and energy dependent character of the self-energy operator Σ these corrections to LDA eigenvalues are also energy dependent.

Table 2. ScN eigenvalues in eV for the valence bands and conduction bands at high symmetry points in LDA and GW calculations.

	LDA	GW		LDA	GW
Γ_1^v	−48.162	−49.842	X_1^v	−48.075	−49.781
Γ_8^v	0.000	0.000	X_8^v	−0.773	−0.893
Γ_1^c	1.99	4.041	X_1^c	−0.108	1.244
Γ_8^c	20.293	22.286	X_8^c	15.606	17.783
W_1^v	−48.072	−49.79	L_1^v	−48.096	−49.813
W_8^v	−2.312	−2.503	L_8^v	−2.458	−2.381
W_1^c	3.056	5.015	L_1^c	3.982	6.625
W_8^c	12.476	13.865	L_8^c	15.23	15.948

Table 3. YN eigenvalues in eV for the valence bands and conduction bands at high symmetry points in LDA and GW calculations

	LDA	GW		LDA	GW
Γ_1^v	−40.539	−41.98	X_1^v	−40.383	−41.892
Γ_8^v	0.000	0.000	X_8^v	−0.361	−0.439
Γ_1^c	2.451	2.797	X_1^c	0.142	0.533
Γ_8^c	23.219	24.405	X_8^c	16.01	17.034
W_1^v	−40.38	−41.912	L_1^v	−40.419	−41.95
W_8^v	−1.413	−1.669	L_8^v	−2.237	−2.484
W_1^c	3.819	4.683	L_1^c	5.384	6.564
W_8^c	13.146	14.209	L_8^c	13.584	14.219

4. Conclusions

An accurate description of the band structure and excitation energies of the transition metal mononitrides, ScN and YN, has been obtained by calculating the self-energy operator within the GW approximation. In our calculations we treat Sc's and Y's semicore electrons as valence electrons. We found that ScN and YN are indirect semiconductors. The band gap of ScN is 1.244 eV, which is in good agreement with the available experimental data, and we predict that the gap of YN is 0.544 eV.

References

[1] Vepřek S and Vac J 1999 *Sci. Technol.* A **17** 2401

[2] Yang H, Al-Brithen H, Smith A R, Borchers J A, Cappelletti R L and Vaudin M D 2001 *Appl. Phys. Lett.* **78** 3860

[3] Madan A, Wang Y, Barnett S A, Engström C, Ljungcrantz H, Hultman L and Grimsditch M 1998 *J. Appl. Phys.* **84** 776

[4] Travaglini G, Marabelli F, Monnier R, Kaldis E and Wachter P 1986 *Phys. Rev.* B **34** 3876

[5] Monnier R, Rhyner J, Rice T M and Koelling D D 1985 *Phys. Rev.* B **31** 5554

[6] Dismukes P J, Yim M W and Ban S V 1972 *J. Cryst. Growth* **13/14** 365

[7] Moustakas T D, Molnar R J and Dismukes J P 1996 *Electrochem. Soc. Proc.* **96**(11) 197

[8] Gall D, Städele M, Järrendahl K, Petrov I, Desjardins P, Haasch R T, Lee T Y and Greene J E 2001 *Phys. Rev.* B **63** 125119

[9] Bai X, Hill D M and Kordesch M E 1999 in *Wide-Bandgap Semiconductors for High-Power, High Frequency and*

High-Temperature and High-Temperature Applications — 1999, edited by Binari S, Burk A, Mollock M and Nguyea C, Symposia M R S Proceedings No. 572 (Pittsburgh: Materials Research Society) p529
[10] Stampfl C, Mannstadt W, Asahi R and Freeman A J 2001 *Phys. Rev.* B **63** 155106
[11] Lambrecht W R L 2000 *Phys. Rev.* B **62** 13538
[12] Perdew J P and Levy M 1983 *Phys. Rev. Lett.* **51** 1884
[13] Lu T Y, Chen D Y and Huang M C 2005 *Chin. Phys. Lett.* **23** 943
[14] Troullier N and Martins J L 1993 *Phys. Rev.* B **43** 1993
[15] Ceperley M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[16] Hedin L 1965 *Phys. Rev.* **139** A796
[17] Hedin L and Lundqvist S in 1969 *Solid State Physics, Advances in Research and Application,* edited by Seitz F, Turnbull D and Ehrenreich H (New York: Academic) **23** p1
[18] Von der Linden W and Horsch P 1988 *Phys. Rev.* B **37** 8351
[19] Louie S G, Froyen S and Cohen M L 1982 *Phys. Rev.* B **26** 1738