

Partial LCAO Densities of States for ScN, TiN, ZrN and ScP

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Densities of states (DOS) and partial densities of states were calculated from self-consistent APW band structure calculations for four transition metal compounds (ScN, TiN, ZrN and ScP) using a recently published improved LCAO interpolation scheme. The total DOS and the LCAO non local partial metal *s*, *p* and *d* and non-metal *s* and *p* DOS of these compounds are presented and compared with non local LCAO partial DOS from earlier calculations as well as with local partial DOS obtained directly from the APW or LAPW wave functions. A LCAO charge analysis for all valence states and for the individual valence bands is also given.

Key words: LCAO interpolation – Partial density of states – Density of states – TiN – ScN – ScP – ZrN.

1. Introduction

In a recent paper [1] an improved LCAO interpolation scheme for transition metal compounds crystallizing in the sodium chloride structure was presented, and optimized LCAO parameter sets based on self-consistent APW band structure calculations [2–4] were published for the four compounds ScN, TiN, ZrN and ScP.

By means of the optimized parameter sets, the density of states (DOS) and LCAO partial densities of states were calculated and will be presented in this paper. LCAO partial densities of states can be very useful for the estimation or calculation of a variety of physical properties such as photoemission spectra [5], optical [6] and magnetic [7] properties.

As described in Ref. [1], the new LCAO basis contains not only Bloch sums originating from orthogonalized non-metal s and p and metal d atomic orbitals (Löwdin orbitals), as earlier LCAO interpolations for these compounds [2, 4], but also Bloch sums originating from metal s and p atomic orbitals. Therefore, we can also present LCAO partial metal s and p DOS in conjunction with partial metal d and non-metal s and p DOS.

2. Calculation of the LCAO Total and Partial Densities of States

Using the optimized LCAO parameter sets of Ref. [1], based on Bloch sums constructed from mutually orthogonalized atomic orbitals, LCAO eigenvalues E_{nk} and corresponding eigenvectors $c_{lm}^t(E_{nk})^*$ were computed for 1378 non-equivalent k points in the irreducible wedge of the Brillouin zone. The DOS was calculated from these energies by means of the method of Gilat and Raubenheimer [8].

The LCAO eigenvectors $c_{lm}^t(E_{nk})$ are normalized to unity in the unit cell for each state E_{nk} . Therefore, the total DOS can be split into partial (l -like) DOS by weighting each state E_{nk} by the sum over m of the square moduli of the corresponding eigenvectors belonging to a certain value of the angular momentum quantum number l :

$$\sum_{m=-l}^l |c_{lm}^t(E_{nk})|^2. \quad (1)$$

For the present LCAO interpolation calculation, the total DOS can be split into five different components: partial non-metal s and p , metal s , p and d DOS:

$$g(E) = g_s^X(E) + g_p^X(E) + g_d^M(E) + g_s^M(E) + g_p^M(E) \quad (2)$$

X : non-metal (N or P)

M : metal (Sc, Ti, Zr).

In Refs. [2, 4], the partial metal s and p DOS are implicitly included in the other LCAO partial DOS.

In crystals of cubic symmetry, the metal d states are further split into states of t_{2g} and e_g symmetry. The partial metal d DOS can be partitioned accordingly into a partial metal t_{2g} and a partial metal e_g DOS. The relative magnitudes of these two components for a given energy may depend on the basis functions used for the interpolation.

The LCAO partial DOS are non-local quantities, contrary to the local partial DOS (sometimes called "character densities" [2]) found by means of band structure calculation methods which use a muffin-tin potential, such as the APW, KKR, LAPW or LMTO method. This means that the LCAO partial DOS refer

* The index t refers to the atomic site where the respective Löwdin orbital, characterized by the angular momentum quantum number l and the magnetic quantum number m , is centred.

to the whole unit cell, contrary to the local partial DOS, which refer to a special muffin-tin sphere.

Summation of the LCAO *l*-like partial DOS over all occupied states below the Fermi level gives partial LCAO *l*-like charges C_l^i which reside in the entire unit cell [2].

3. Presentation of Data

Figure 1 shows the total LCAO densities of states for ScN, TiN, ZrN and ScP. The LAPW DOS for ZrN from Ref. [3] is also displayed in this figure.

Figure 2 presents the “large components” of the LCAO partial DOS for the four above-mentioned compounds (i.e. the partial non-metal *s* and *p* and metal *d* DOS).

Figure 3 gives the “small components”, i.e. the partial metal *s* and *p* DOS.

Figure 4 presents, finally, the decomposition of the partial metal *d* DOS into the components of t_{2g} and e_g symmetry.

The DOS for all four compounds are rather similar. Above the lowest valence band formed by states of mainly non-metal *s* character (“*s* band”), three bands are found, whose states exhibit mostly non-metal *p* symmetry (“*p* band”). Large contributions to the *p* band come also from states of predominantly metal *d* character. The degree of mixing of non-metal *p* and metal *d* states in the *p* band can be regarded as a measure for the strength of covalent *p*-*d* binding between nearest neighbors in the crystal.

The DOS in the *p* band is split more or less distinctly into two peaks. Separated by a pronounced minimum, a set of five bands of mainly metal *d* character, but

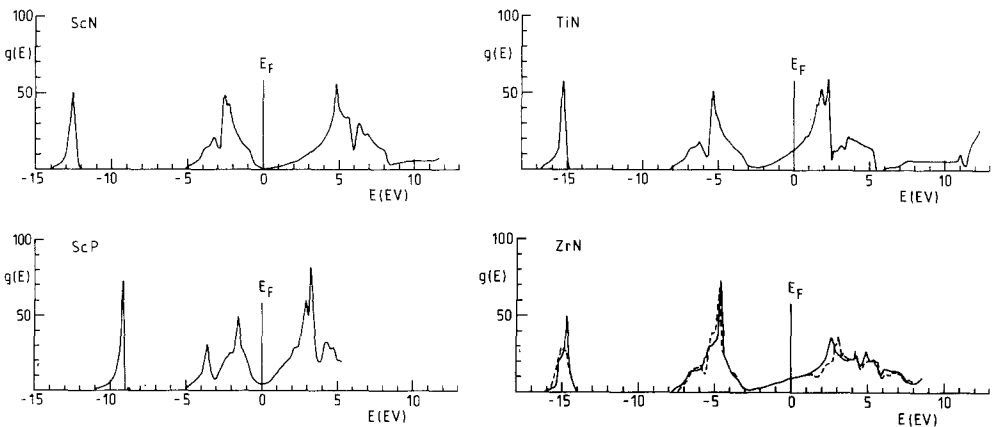


Fig. 1. Total densities of states for ScN, TiN, ZrN and ScP in states of both spin directions per Ryd and unit cell. The energy zero is positioned at the Fermi level of the respective compound. For ZrN the LAPW DOS of Ref. [3] is also shown (---)

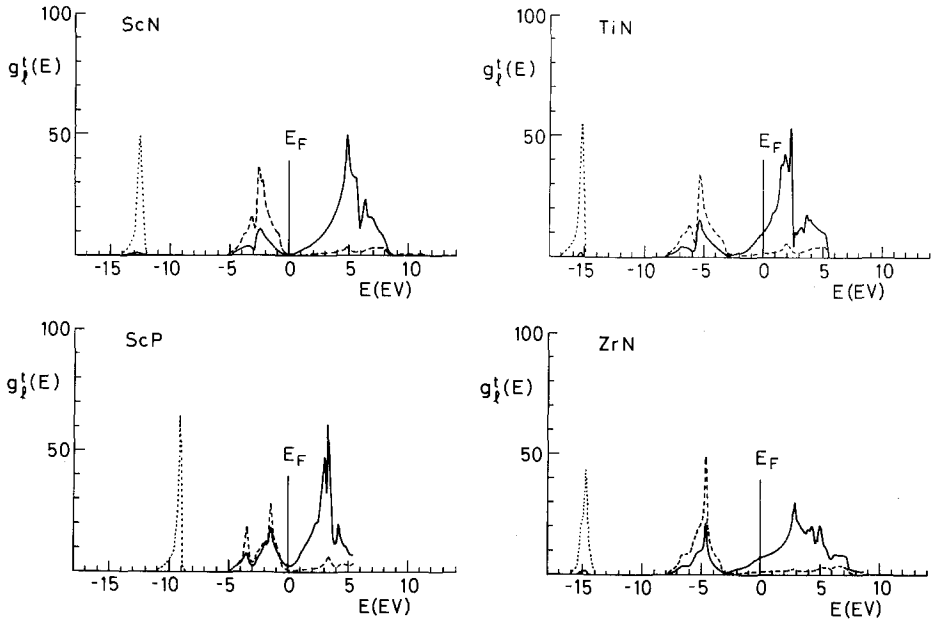


Fig. 2. "Large" components of the LCAO partial densities of states for ScN, TiN, ZrN and ScP in states of both spin directions per Ryd and unit cell. The energy zero is positioned at the Fermi level of the respective compound. — metal d DOS (g_d^M); --- non-metal p DOS (g_p^X); ···· non-metal s DOS (g_s^X)

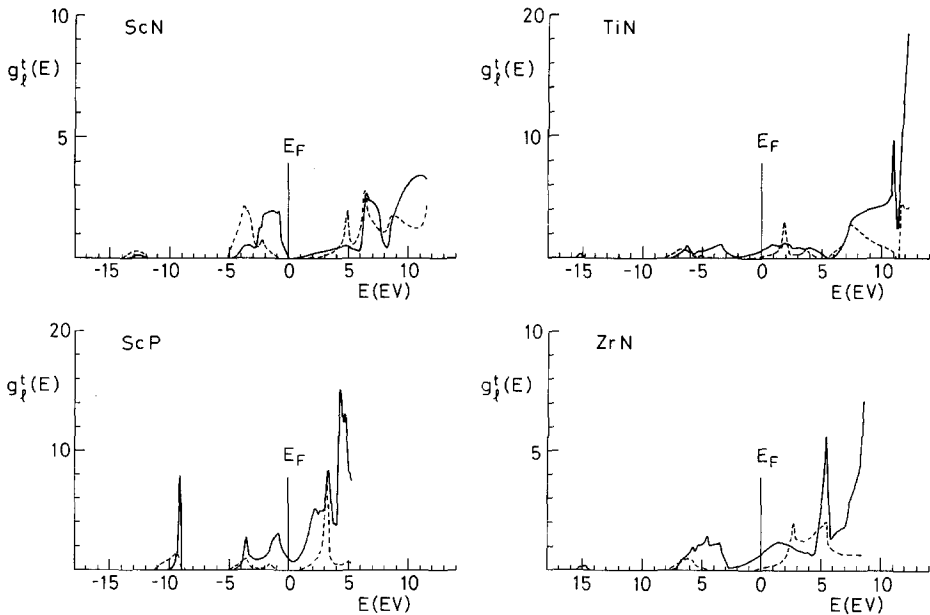


Fig. 3. "Small" components among the LCAO partial DOS for ScN, TiN, ZrN and ScP in states of both spin directions per Ryd and unit cell. The energy zero is positioned at the Fermi level of the respective compound. — metal s DOS (g_s^M); --- metal p DOS (g_p^M)

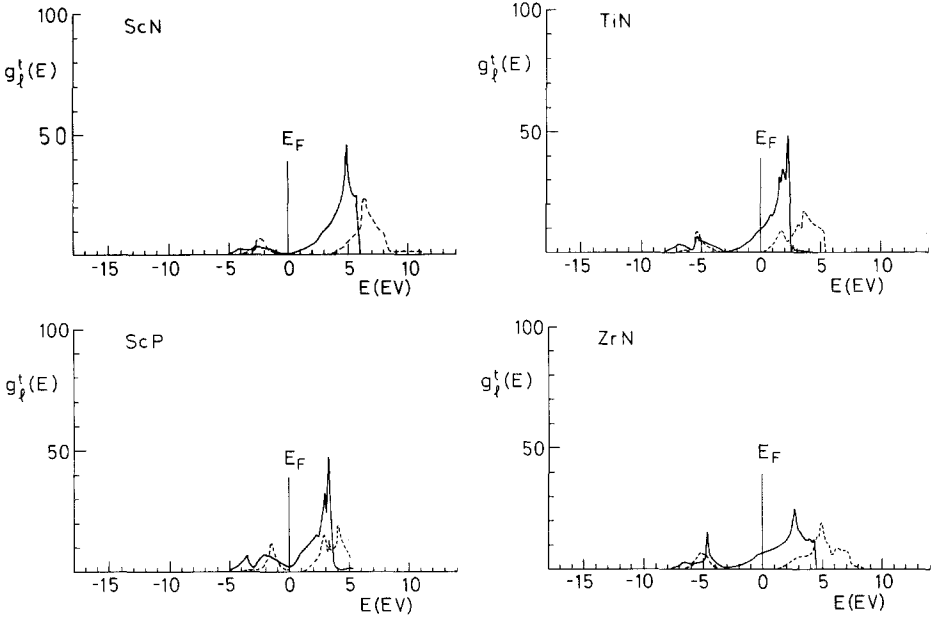


Fig. 4. Splitting of the metal d DOS in components of t_{2g} and of e_g symmetry. Partial DOS are given in states of both spin directions per Ryd and unit cell. The energy zero is positioned at the Fermi level of the individual compound. — metal t_{2g} DOS ($g_{t_{2g}}^M$); --- metal e_g DOS ($g_{e_g}^M$)

with a strong component of states of non-metal p symmetry, follows in the energy scale. This set is known as the “ d band”. It represents metal–metal bonding interactions, mainly between states of t_{2g} symmetry, and metal non-metal antibonding interactions. The d band is followed by a set of rather free-electron like bands with a large fraction of metal s and metal p character (“metal s - p band”). The Fermi level E_F for ScN and ScP lies in the minimum between the p and d band, whereas the Fermi level for TiN and ZrN lies within the d band. Table 1 shows the Fermi energy and the DOS and partial DOS values at the Fermi level.

Table 1. APW and LCAO Fermi level E_F (in Ryd) and total and partial densities of states at $E = E_F$ (in states of one spin direction per eV and unit cell)

Compound MX	ScN	TiN	ZrN	ScP
E_F^{APW}	0.566	0.778	0.796	0.460
E_F^{LCAO}	0.562	0.790	0.802	0.466
$g(E_F)$	0.025	0.432	0.341	0.157
$g_s^X(E_F)$	0	0.002	0.000	0
$g_p^X(E_F)$	0.013	0.059	0.051	0.030
$g_{t_{2g}}^M(E_F)$	0.007	0.333	0.256	0.082
$g_{e_g}^M(E_F)$	0.000	0.012	0.005	0.011
$g_s^M(E_F)$	0	0.005	0.003	0.000
$g_p^M(E_F)$	0.005	0.024	0.026	0.035

For the comparison with the values of Ref. [2] see footnote² on p. 139.

An extensive discussion of bonding in transition metal compounds is found in Refs. [3, 9, 10].

Table 2 presents the partial LCAO charges C_i^l found by summation of the partial DOS for a particular l over all occupied states. The so-called band charges are also tabulated: they result from the summation of the partial DOS for a specific

Table 2. Partial LCAO charges C_i^l in number of electrons per unit cell

	ScN	TiN	ZrN	ScP
<i>Non-metal s band</i>				
C_s^X	1.92 [91%]	1.94 [97%]	1.89 [94.5%]	1.73 [86.5%]
C_p^X	0.01 [0.05%]	0.00	0.02 [1%]	0.00
C_d^M	0.05 [2.5%]	0.04 [2%]	0.07 [4%]	0.01 [0.5%]
C_s^M	0.02 [1%]	0.01 [0.5%]	0.01 [0.5%]	0.13 [6.5%]
C_p^M	0.01 [0.5%]	0.01 [0.5%]	0.01 [0.5%]	0.13 [6.5%]
C_{12p}^M	0.01 [0.5%]	0.00	0.01 [0.5%]	0.01 [0.5%]
C_{eg}^M	0.04 [2%]	0.04 [2%]	0.06 [3.5%]	0.00
Number of e^- in the band	2.00 [100%]	2.00 [100%]	2.00 [100%]	2.00 [100%]
<i>Non-metal p band</i>				
C_s^X	0.01	0.01	0.06 [1%]	0.00
C_p^X	4.15 [69%]	3.93 [66%]	3.89 [65%]	3.08 [51%]
C_d^M	1.23 [20%]	1.72 [29%]	1.74 [29%]	2.34 [39%]
C_s^M	0.29 [5%]	0.09 [1%]	0.06 [1%]	0.11 [2%]
C_p^M	0.33 [6%]	0.23 [4%]	0.25 [4%]	0.47 [8%]
C_{12p}^M	0.62 [10%]	1.06 [18%]	1.04 [17%]	1.55 [26%]
C_{eg}^M	0.61 [10%]	0.66 [11%]	0.70 [12%]	0.79 [13%]
Number of e^- in the band	6.00 [100%]	6.00 [100%]	6.00 [100%]	6.00 [100%]
<i>Occupied part of the metal d band</i>				
C_s^X	(0.00)	0.00	0.00	(0.00)
C_p^X	(0.11)	0.19	0.22	(0.13)
C_d^M	(0.85)	0.75	0.70	(0.73)
C_s^M	(0.01)	0.01	0.00	(0.01)
C_p^M	(0.03)	0.05	0.07	(0.13)
C_{12p}^M	(0.85)	0.73	0.69	(0.69)
C_{eg}^M	(0)	0.02	0.01	(0.04)
Number of e^- in the band	(1.00)	1.00	1.00	(1.00)
<i>All valence states</i>				
C_s^X	1.93 [24%]	1.95 [22%]	1.95 [22%]	1.73 [22%]
C_p^X	4.16 [52%]	4.12 [46%]	4.13 [46%]	3.08 [38%]
C_d^M	1.28 [16%]	2.52 [28%]	2.52 [28%]	2.35 [29%]
C_s^M	0.29 [4%]	0.11 [1%]	0.07 [1%]	0.24 [3%]
C_p^M	0.33 [5%]	0.29 [3%]	0.33 [3%]	0.60 [8%]
C_{12p}^M	0.63 [8%]	1.8 [20%]	1.74 [19%]	1.56 [19%]
C_{eg}^M	0.65 [8%]	0.72 [8%]	0.78 [9%]	0.79 [10%]
Valence electron concentration (VEC)	8.00 [100%]	9.00 [100%]	9.00 [100%]	8.00 [100%]

l value over all states of a particular valence band¹. In the next paragraph these quantities will be compared to local partial charges found from the corresponding local APW partial DOS.

4. Comparison with Partial Densities of States Resulting from Earlier Calculations

One can compare the present partial DOS with partial DOS based on earlier LCAO calculations [2, 4] using the same (or in the case of TiN a very similar) APW band structure². Thereby one recognizes agreement in the main features of the diagrams (band positions and band widths) within the range of the interpolation errors (up to 2×10^{-2} Ryd). Due to these interpolation errors, the "fine structure" of the total DOS is however slightly different for the two different LCAO interpolations, as well as for the LCAO and LAPW DOS of ZrN. In this case, there was also a coarser k grid used for the calculation of the LAPW DOS. The LCAO non-metal s band of ZrN is, for example, narrower by about 0.02 Ryd than for the APW and LAPW calculation, as can be deduced from Fig. 2 of Ref. [1], which shows the LCAO and APW band structure of ZrN.

When comparing the LCAO partial DOS with their earlier counterparts, additional differences arise. The reason for this is that the partial non-metal s and p and metal d DOS of Refs. [2] and [4] contain implicitly the metal s and p components, which are separately treated in the present calculation. The two sets of LCAO partial DOS for ScN and TiN are shown to be rather similar. If the partial metal $4s$ and $4p$ DOS components are treated separately, as in the present calculation, the other partial DOS components diminish accordingly when compared to the earlier calculations; since the partial DOS presented in this paper contain no longer implicitly the contributions of metal $4s$ and $4p$ states. This effect becomes, of course, more pronounced for higher energies where hybridization, or even overlap of the d band with the metal s - p band, occurs. The present calculation shows, for example, that the partial N s and a large fraction of the N p DOS at the top of the d band, which are found in Refs. [2, 4], actually originate from metal $4s$ and metal $4p$ states.

No earlier LCAO interpolation calculation was published for ZrN.

As for ScP, the present calculation reveals a not insignificant Sc $4s$ and Sc $4p$ partial DOS even for relatively low energies below the Fermi level. In Ref. [4]

¹ For ScN and ScP, whose Fermi level lies in the minimum between p and d band, the partial charges for the occupied fraction of the d band are hypothetical values. They are obtained by assuming that one additional valence electron is filled into the energetically lowest states of the unoccupied Sc d band.

² The total and partial DOS values of Refs. [2, 4] should be multiplied by a factor $F = a_0^3/16\pi^3$ (a_0 : lattice parameter in a.u.) which has erroneously not been taken into account in these calculations.

F values for various compounds:

TiC: 1.10277	ScN: 1.1985	VC: 0.99491
TiN: 1.0383	ScO: 1.1985	VN: 0.96526
TiO: 0.99123	ScP: 2.0390	VO: 0.93289

a relatively large component of Sc e_g states was found in the P 3s band in place of contributions of Sc s and Sc p states obtained in the present calculation.

When comparing the partial LCAO DOS with the APW local partial DOS calculated from the same APW band structure, the general features of the curves are again similar but the “fine structure” shows slight differences which can be attributed to several causes:

a) As already mentioned, the APW partial DOS are local quantities. After summing them over all occupied states, local partial charges result which refer only to an individual muffin-tin sphere, whereas after summation over the LCAO partial DOS for all occupied states, partial LCAO charges residing in the *entire unit cell* are obtained. The ratio between components of different symmetry for a given energy can be different for local and non-local partial DOS, as the amount of charge residing outside the muffin-tin spheres for states of different l depends upon the degree of localization of the respective orbitals and upon the energy.

b) The APW local partial DOS are calculated only from eigenvalues and wave functions for a small number of k points in the irreducible wedge of the Brillouin zone. Therefore, they can only be given in crude histogram form. The shape of these histograms can also depend on the size of the energy interval used for the calculation of the histogram.

c) Due to deviations of the interpolated LCAO energies from the APW energies, which are sometimes as large as 0.02 Ryd, the LCAO partial DOS are based on a band structure slightly different from its APW counterpart (see Figs. 1 to 4 of Ref. [1]). The partial LCAO band charges of Table 2 can be compared with APW or LAPW local partial charges as found for ScN[2], TiN[2], ZrN[3] and ScP[4]. Being localized in the respective muffin-tin spheres, the local partial APW or LAPW charges are always smaller than their LCAO counterparts. The greatest discrepancies occur with respect to the metal d charges. For ScP, for example, the LCAO calculation gives 2.34 Sc d electrons in the unit cell, whereas the APW local d charge in the Sc d sphere does not exceed 1.04 electrons. For TiN a detailed LAPW charge analysis exists [10], wherein the Ti t_{2g} and e_g partial charges in the Ti sphere are tabulated separately for the p band and the occupied fraction of the d band. A comparison of these values with their LCAO counterparts shows that the large difference between local and non-local partial Ti d charge is due to the fact that a large fraction of the Ti t_{2g} charge in the p band resides outside the Ti muffin-tin sphere. This effect is particularly pronounced in the [110] direction where titanium–nitrogen d - $p\pi$ bonding occurs.

5. Conclusion

The LCAO partial DOS presented in this paper for ScN, TiN, ZrN and ScP are based on a LCAO interpolation of APW band structures. The interpolated LCAO eigenvalues differ maximally 0.02 Ryd from the corresponding APW energies. The LCAO partial DOS are non-local quantities which do not depend

upon the size of the muffin-tin spheres, as do their local APW or LAPW counterparts.

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