Theoret. Chim. Acta (Berl.) 60, 313–325 (1981)

THEORETICA CHIMICA ACTA

An Improved LCAO Interpolation Scheme for Energy Band Structures. Application to Four Compounds (ScN, ScP, TiN, ZrN) Crystallizing in the Sodium Chloride Structure

Michael Dorrer, Renate Eibler, and Adolf Neckel

Institut für physikalische Chemie der Universität Wien, Währingerstraße 42 A-1090 Wien, Austria

An improved version of the LCAO interpolation scheme using metal *s*-, *p*-, *d*-, and non metal *s*-, and *p*-basis functions is presented for transition metal compounds with sodium chloride structure. This method enables us to interpolate with reasonable accuracy occupied bands as well as unoccupied energy bands up to 0.9 Rydberg above the Fermi level for the compounds ScN, ScP, TiN and ZrN. Due to the limited basis, problems arise however with bands of predominantly transition metal *f* or non metal *d* character lying in this energy range – as is the case for ScP.

Optimized parameter sets are presented for the compounds ScN, ScP, TiN and ZrN. They were used for the calculation of the imaginary part of the complex dielectric function, $\varepsilon_2(\omega)$, as will be shown in two forthcoming papers.

Key words: LCAO interpolation – TiN – ZrN – ScN – ScP.

1. Introduction

Recently reliable measurements of the optical reflectivity were performed for TiN[1], ZrN[1], ScN[2] and ScP[2] and curves of the imaginary part of the complex dielectric function, $\varepsilon_2(\omega)$, were reported.

If one assumes that excited states in a solid can be approximatively described by unoccupied ground state one electron energies and corresponding wave functions, it is in principle possible to calculate the interband contribution to $\varepsilon_2(\omega)$ using ground state band structure energy levels and to compare the results with the measured curves [3].

0040-5744/81/0060/0313/$02.60

For the four compounds mentioned above, which crystallize in the sodium chloride structure, self consistent ground state APW energies are available for 29 nonequivalent $\boldsymbol{k}$ points in the irreducible wedge of the first Brillouin zone [4–7]. This number of $\boldsymbol{k}$-points is of course not sufficient for a precise integration over the Brillouin zone which, however, is necessary for calculating $\epsilon_2(\omega)$.

Therefore an interpolation scheme generating additional energies at a sufficient high number of $\boldsymbol{k}$ points is needed. As the $\varepsilon_2(\omega)$ measurements cover an energy range of 0.03 to 12 eV, states up to 0.9 Rydberg above the Fermi level have to be included. This means interpolation of mostly ten, in some cases even eleven valence bands.

For the calculation of the density of (mainly occupied) states of the four compounds an LCAO interpolation scheme following Slater and Koster [8] using a basis of nine Bloch sums constructed from mutually orthogonalized metallic d and non metallic s and p atomic orbitals had been used and had given satisfactory results for at least the occupied valence bands. If, however, higher bands overlapped the metallic d bands as was the case for ScP and ZrN the fit of the ninth band was not very good. The nine Bloch sums basis is of course not able to reproduce more than nine bands. Therefore the existing LCAO interpolation program had to be extended by including additional Bloch sums formed from metallic s and p atomic orbitals in the basis which now contains thirteen Bloch sums.

This necessary extension produced however serious numerical problems connected with the search for good starting values for the LCAO parameters and with the convergence of the optimizing procedure.

Therefore some modifications of the routine were made. As these may be of interest to other users of interpolation programs they will be published in this paper together with the optimized parameter sets for TiN, ZrN, ScN and ScP. Later publications will contain the results of the $\varepsilon_2(\omega)$ calculations for TiN and ZrN [15], and the corresponding results for ScN and ScP [16].

2. The LCAO Interpolation Scheme

2.1. Short Description of the Method

The LCAO interpolation scheme as proposed by Slater and Koster [8] and applied to refractory compounds has already been described elsewhere [7, 9]. However, for sake of clarity the principal facts will be displayed once more.

The LCAO interpolation wave function for a solid is a linear combination of Bloch sums $\chi_i(\boldsymbol{k}, \boldsymbol{r})$ constructed by applying the projection operator for the irreducible representation $\boldsymbol{k}$ of the translational group to atomic orbitals $\phi_i(\boldsymbol{r})$. The index i and j respectively, indicates both the form of the function (orbital and magnetic quantum number (lm) of the orbital) and which type of atom it is centred on. If orthogonalized Bloch sums are required, Löwdin orbitals $\psi_i(\boldsymbol{r})$

instead of atomic orbitals are used in the sum. They are formed from the respective atomic orbitals by the so called symmetric Löwdin orthogonalization [10].

Matrix elements of the Hamiltonian between two Bloch sums are a sum of energy integrals $E_{i,j}(\boldsymbol{t}_{n''}+\boldsymbol{T}_{ij})$, the so-called LCAO parameters:

$$\begin{aligned}\langle\chi_i(\boldsymbol{k},\boldsymbol{r})|\mathscr{H}|\chi_j(\boldsymbol{k},\boldsymbol{r})\rangle &= (1/{}^oT)\sum_{\boldsymbol{t}_{n'}\in T}\exp\left(i\boldsymbol{k}\cdot(\boldsymbol{t}_{n'}+\boldsymbol{T}_{ij})\right)\langle\psi_i(\boldsymbol{r})|\mathscr{H}|\psi_j(\boldsymbol{r}-\boldsymbol{t}_{n'}-\boldsymbol{T}_{ij})\rangle\\ &= \sum_{\boldsymbol{t}_{n'}\in T}\exp\left(i\boldsymbol{k}(\boldsymbol{t}_{n'}+\boldsymbol{T}_{ij})\right)E_{i,j}(\boldsymbol{t}_{n'}+\boldsymbol{T}_{ij}) \qquad (1)\end{aligned}$$

${}^oT$ is the order of the translational group.

The sum in Eq. (1) extends over all lattice translations $\boldsymbol{t}_n$. $\boldsymbol{T}_{ij}$ is the distance between the lattice sites i and j in the same unit cell. The energy integrals $E_{i,j}(\boldsymbol{t}_n+\boldsymbol{T}_{ij})$ between a Löwdin orbital centred at the lattice site i and another orbital centred at another site j at a distance $\boldsymbol{t}_n+\boldsymbol{T}_{ij}$ from it are determined by a non-linear least squares procedure fitting the eigenvalues of the LCAO Hamiltonian matrix $\boldsymbol{H}(\boldsymbol{k})$ to the known APW energies at $\boldsymbol{k}$ points belonging to the set of 29.

To start the fitting procedure it is necessary to assume some starting values for the energy integrals which will now be called LCAO parameters Q_j. The numbers j characterizing the various energy integrals are listed in the second column of Table 1. The right choice of starting values for the parameters is one of the critical points for the usefulness of the method.

The non linear least squares procedure converges finally to an optimized LCAO parameter set which is used for generating and diagonalizing the Hamiltonian matrix $\boldsymbol{H}$ at as many $\boldsymbol{k}$ points as required for an accurate Brillouin zone integration (density of states, joint density of states, $\varepsilon_2(\omega)$).

2.2. Difficulties and Restrictions of the Conventional LCAO Interpolation Method

In principle the search for the best LCAO parameters may be undertaken in two slightly different ways: firstly one can use the unsymmetrized LCAO matrix and calculate its eigenvalues for all $\boldsymbol{k}$ points with known APW energies [7, 9]. In this case the choice of the starting values for the LCAO parameters is rather critical: the LCAO matrix has the same dimension as the total number of basis functions and the LCAO parameters very often do not converge at all or converge to unphysical parameter sets, especially when the starting values for the parameters are far away from the optimal values.

With few basis functions one can find in most cases suitable starting values for the parameters by the following method: by an unitary transformation the n-dimensional LCAO matrix splits for a symmetry point $\boldsymbol{k}_j$ in several lower-dimensioned submatrices belonging to various irreducible representations of the point group of $\boldsymbol{k}_j$. If n is not bigger than nine (as with the LCAO interpolation used before) some of these irreducible submatrices are only one- or two-dimensional. If the unknown eigenvalues of these small submatrices are replaced by the known corresponding APW energies, linear and quadratic equations for the parameters result. The solutions of these equations are then used as starting values for the parameters in an unsymmetrized LCAO calculation.

If, however, more basis functions have to be taken, as in the present case, most of the irreducible submatrices are higher dimensioned and there are not sufficient linear and quadratic equations available for all important parameters. This may very well be one of the main reasons why the LCAO interpolation was said to be unable to fit the unoccupied bands fairly above the Fermi level [11].

Another general problem when using the LCAO interpolation with an unsymmetrized basis lies in the fact that the correct ordering of the LCAO energies with respect to the APW energies is not guaranteed. Only if the main l-like component of the LCAO wave function corresponds to the principal l-like component of the corresponding APW wave function the LCAO parameters have converged to "physically" and not only numerically optimized values.

For determining the optimized parameter sets the LCAO as well as the APW energies for each $\boldsymbol{k}$ point are arranged in increasing magnitude and then equalized. Especially when using bad starting values, it may happen with this method that an LCAO eigenvalue belonging in principle to an irreducible representation μ, which is of course unknown to the unsymmetrized program, is fitted to an APW energy belonging to a different irreducible representation μ'. In this case the LCAO parameters do not converge or reach only an unphysical minimum.

Because of these difficulties some authors use a symmetrized version of the LCAO interpolation scheme [12, 13].

When applying at a symmetry point $\boldsymbol{k}_j$ projection operators for the irreducible representations μ of the point group of the wave vector $\mathcal{G}_{\boldsymbol{k}_j}$ to the LCAO wave functions composed of Bloch sums $\chi_i(\boldsymbol{k}, \boldsymbol{r})$ a new symmetrized basis $\chi'(\boldsymbol{k}, \boldsymbol{r})$ is generated. $\chi'(\boldsymbol{k}, \boldsymbol{r})$ results also if the Hamiltonian matrix $\boldsymbol{H}$ in the basis χ is submitted to a similarity transformation by the unitary matrix $\boldsymbol{U}$:

$$\boldsymbol{H}' = \boldsymbol{U}^{+}\boldsymbol{H}\boldsymbol{U} \tag{2}$$

$$\chi = \chi\boldsymbol{U} \tag{3}$$

In the symmetrized basis $\boldsymbol{H}'$ splits into submatrices belonging to the various irreducible representations of $\mathcal{G}_{\boldsymbol{k}_j}$. The LCAO eigenvalues are now separately found for each irreducible submatrix and can be fitted to the APW eigenvalues belonging to the same irreducible representation.

The various LCAO submatrices in three symmetry directions of the NaCl structure ([100], [110], [111]) for the different irreducible representations of $\mathcal{G}_{\boldsymbol{k}_j}$ are given analytically by Honig and Wahnsiedler [13]. Their Bloch sums are however not normalized. Therefore, some of their rows and columns must be divided by a constant factor. The irreducible submatrices for the point W ($\boldsymbol{k}_j = (048)\frac{\pi}{4a}$; a: lattice parameter) missing in Ref. [13], are listed in Appendix A of the present paper.

When using the symmetrized version of the LCAO interpolation scheme the LCAO eigenvalues are always fitted to the APW energies with the same symmetry properties. Therefore, the main l-like component of the LCAO wavefunction is the same as in the APW calculation. In this case the choice of starting values for the parameters is not so critical for the right convergence of the fitting procedure.

There are, however, also disadvantages when using the symmetry-adapted LCAO basis. The irreducible LCAO submatrices must be set up separately for each symmetry point $\boldsymbol{k}_j$ or symmetry direction. They are not defined for general $\boldsymbol{k}$ points or even symmetry planes. Therefore when determining optimized values only a small number of all the known APW energies can be actually used (the $29\boldsymbol{k}$ point mesh contains some general $\boldsymbol{k}$ points and many $\boldsymbol{k}$ points situated only on symmetry planes).

Finally, when calculating densities of states, $\varepsilon_2(\omega)$ or other Brillouin zone integrals, a different routine must be used to find LCAO eigenvalues and eigenvectors for arbitrary and general $\boldsymbol{k}$ points.

2.3. *Short Description of the Modified* LCAO *Calculations*

The modified version of the LCAO interpolation scheme, which we used for calculating the LCAO energies needed for the computation of $\varepsilon_2(\omega)$, combines the advantages of the symmetrized and non-symmetrized version.

As already mentioned thirteen Bloch sums originating from metallic s, p, and d Löwdin orbitals $[s_M, p_M, d_M]$ and from non metallic s and p Löwdin orbitals $[s_N, p_N]$ were included in the basis. For every $\boldsymbol{k}$ the full unsymmetrized 13×13 Hamiltonian matrix is set up. When the program encounters a symmetry point $\boldsymbol{k}_j$ a special procedure assures that all the LCAO energies for this point belonging to a special irreducible representation of $\mathscr{G}_{\boldsymbol{k}_j}$ are fitted to the APW eigenvalues belonging to the same irreducible representation.

The matrix elements of the Hamiltonian between two Bloch sums depend linearly on the LCAO parameters Q_j. The dependency of the energy eigenvalues on Q_j is given by the Hellman-Feynman theorem [14]:

$$\frac{\partial E_n^{\mathrm{LCAO}}(\boldsymbol{k})}{\partial Q_j} = \boldsymbol{C}_n^+(\boldsymbol{k}) \frac{\partial H(\boldsymbol{k})}{\partial Q_j} C_n(\boldsymbol{k}) \tag{4}$$

This is no longer a linear dependence because the eigenvectors $\boldsymbol{C}_n(\boldsymbol{k})$ depend on the parameters Q_j as well.

By inspection of the *symmetrized* LCAO submatrices in [13] and also of Appendix A one finds almost for every symmetry point $\boldsymbol{k}_j$ a special parameter $Q_{j'}$ only appearing in the diagonal element $H^{\mu'}_{mm}(\boldsymbol{k}_j)$ of a submatrix belonging to a special irreducible representation μ'. In this case the matrix $(\partial \boldsymbol{H}(\boldsymbol{k}_j)/\partial Q_{j'})$ contains besides the diagonal element $(\partial H^{\mu'}_{mm}(\boldsymbol{k}_j)/\partial Q_{j'})$ only zeros. Therefore:

$$\frac{\partial E_n(\boldsymbol{k}_j)}{\partial Q_{j'}} = \boldsymbol{C}_n^+(\boldsymbol{k}_j)\frac{\partial \boldsymbol{H}(\boldsymbol{k}_j)}{\partial Q_{j'}}\boldsymbol{C}_n(\boldsymbol{k}_j) = c_m(\boldsymbol{k}_j)^2\frac{\partial H^{\mu'}_{mm}(\boldsymbol{k}_j)}{\partial Q_{j'}} \tag{5}$$

and:

$$\operatorname{sign}\left[\frac{\partial E_n(\boldsymbol{k}_j)}{\partial Q_{j'}}\right] = \operatorname{sign}\left[\frac{\partial H^{\mu'}_{mm}(\boldsymbol{k}_j)}{\partial Q_{j'}}\right]$$

$E_n(\boldsymbol{k}_j)$ belongs to the irreducible representation μ' of $\boldsymbol{G}_{\boldsymbol{k}_j}$. (For parameters appearing in the non diagonal elements of $\boldsymbol{H}$ the sign cannot be predicted as it depends upon the signs and relative magnitudes of the coefficients $c_n(\boldsymbol{k})$.)

Now for each of the thirteen eigenvalues $E_i(\boldsymbol{k}_j)$ of the *unsymmetrized* LCAO Hamiltonian matrix one asks if

$$\frac{\partial E_i(\boldsymbol{k}_j)}{\partial Q_{j'}} \neq 0 \qquad \text{and} \qquad \operatorname{sign}\left[\frac{\partial E_i(\boldsymbol{k}_j)}{\partial Q_{j'}}\right] = \operatorname{sign}\left[\frac{\partial E_n(\boldsymbol{k}_j)}{\partial Q_{j'}}\right].$$

If these two conditions are fulfilled for an eigenvalue $E_{i'}(\boldsymbol{k}_j)$ than $E_{i'}(\boldsymbol{k}_j)$ corresponds to the eigenvalue $E_n(\boldsymbol{k}_j)$ of the symmetrized LCAO matrix and belongs therefore as well as the latter to the irreducible representation μ' of $\boldsymbol{G}_{\boldsymbol{k}_j}$. Accordingly it must be fitted to the APW energy for this special irreducible representation.

An example of this symmetry control method is given in appendix B for $\boldsymbol{k}_j = W$. Possible extensions are there discussed as well.

For the four substances investigated in this paper the symmetry control described above enabled us to use estimated starting values of the parameters to begin the iteration cycle. We took mean values of the l-like s-, p- and d-bands for the "orbital" parameters $E_{i,i}(000)$ and an arbitrary value of 0.05 for the more important parameters. Energy integrals which we supposed to be small were set to zero. With this set of starting values the parameters converged reasonably fast to physically meaningful values.

We used a total of 45 parameters taking thirteen Bloch sums, including interactions up to third-nearest neighbours. (When using nine Bloch sums and including interactions up to fifth nearest neighbours a total of 41 parameters results, as for example in Ref. [7]).

In the following paragraph the optimized LCAO parameters for TiN, ZrN, ScN and ScP are presented and discussed.

3. Optimized LCAO Parameter Sets for TiN, ZrN, ScN and ScP

Table 1 shows the optimized LCAO parameter sets for TiN, ZrN, ScN and ScP together with the root mean square and the largest deviation of the corresponding

Table 1. LCAO parameters in Rydberg corresponding to the best fit to the self consistent APW energies for TiN, ZrN, ScN and ScP. Deviations between LCAO and APW energies are summarized at the bottom of the table. The parameter values are given with respect to the constant muffin tin potentials of the individual compounds.

Name of energy integral used as parameter	Nomenclature used in computer program and in appendices A and B	Values for			
		TiN	ZrN	ScN	ScP
$E_{s_N,s_N}(000)$	Q_1	−0.300472	−0.225952	−0.311885	−0.052082
$E_{s_N,s_N}(110)$	Q_2	−0.011115	−0.009616	−0.002374	0.004121
$E_{s_N,x_N}(110)$	Q_3	−0.001646	0.008076	−0.009992	0.015402
$E_{s_N,xy_M}(111)$	Q_4	−0.010845	0.010670	−0.011028	−0.018186
$E_{s_N,(3z^2-r^2)_M}(001)$	Q_5	0.072098	0.088562	0.077975	0.002615
$E_{s_N,s_M}(100)$	Q_6	−0.032451	−0.003060	−0.055251	−0.135479
$E_{s_N,s_M}(111)$	Q_7	0.017985	0.032143	−0.009019	0.024491
$E_{s_N,x_M}(100)$	Q_8	0.013841	0.027127	−0.037947	−0.101387
$E_{s_N,x_M}(111)$	Q_9	−0.020105	−0.019375	−0.015336	0.025448
$E_{x_N,x_N}(000)$	Q_{10}	0.686648	0.726504	0.688497	0.642561
$E_{x_N,x_N}(110)$	Q_{11}	0.034449	0.033350	0.042520	0.057136
$E_{x_N,x_N}(011)$	Q_{12}	0.005709	0.018661	−0.000048	0.020375
$E_{x_N,y_N}(110)$	Q_{13}	−0.005397	0.010339	−0.019819	−0.011130
$E_{x_N,xy_M}(010)$	Q_{14}	0.096672	0.104343	0.074280	0.100036
$E_{x_N,xy_M}(111)$	Q_{15}	−0.002954	−0.000460	−0.002842	−0.002139
$E_{x_N,yz_M}(111)$	Q_{16}	−0.006271	−0.000939	−0.004421	−0.008563
$E_{z_N,(3z^2-r^2)_M}(001)$	Q_{17}	0.145748	0.170906	0.144780	0.105882
$E_{x_N,(x^2-y^2)_M}(111)$	Q_{18}	−0.001279	−0.002054	0.007345	0.001811
$E_{x_N,s_M}(100)$	Q_{19}	−0.142766	−0.114195	−0.173007	−0.128831
$E_{x_N,s_M}(111)$	Q_{20}	0.013615	−0.007939	0.006950	0.015792
$E_{x_N,x_M}(111)$	Q_{21}	0.108635	0.135951	0.216247	0.093145
$E_{y_N,y_M}(100)$	Q_{22}	0.105492	0.107924	0.082365	0.065059
$E_{x_N,x_M}(111)$	Q_{23}	−0.014292	−0.008536	−0.000194	−0.016760
$E_{x_N,y_M}(111)$	Q_{24}	−0.006514	0.002698	−0.008441	−0.004765
$E_{xy_M,xy_M}(000)$	Q_{25}	0.810386	0.885294	0.829359	0.587870
$E_{xy_M,xy_M}(110)$	Q_{26}	−0.038183	−0.061192	−0.041400	−0.028962
$E_{xy_M,xy_M}(011)$	Q_{27}	0.012335	0.015403	0.012856	0.007114
$E_{xy_M,xz_M}(011)$	Q_{28}	0.014417	0.010291	0.013585	0.008180
$E_{xy_M,(3z^2-r^2)_M}(110)$	Q_{29}	−0.010409	−0.018236	−0.012451	−0.012831
$E_{xy_M,s_M}(110)$	Q_{30}	0.006977	0.010719	−0.016738	0.015681
$E_{xy_M,x_M}(110)$	Q_{31}	0.024344	0.037528	0.001042	0.012245
$E_{xy_M,x_M}(011)$	Q_{32}	−0.020799	−0.020981	−0.006825	−0.015847
$E_{(3z^2-r^2)_M,(3z^2-r^2)_M}(000)$	Q_{33}	0.939282	1.021411	0.959335	0.691545
$E_{(3z^2-r^2)_M,(3z^2-r^2)_M}(110)$	Q_{34}	−0.002809	−0.004961	−0.003252	−0.000707
$E_{(x^2-y^2)_M,(x^2-y^2)_M}(110)$	Q_{35}	−0.015188	−0.011882	−0.017136	−0.019278
$E_{(3z^2-r^2)_M,s_M}(110)$	Q_{36}	0.010475	−0.018027	−0.023526	0.018324
$E_{(3z^2-r^2)_M,z_M}(011)$	Q_{37}	−0.003841	−0.019558	0.004993	−0.013056
$E_{(x^2-y^2)_M,z_M}(011)$	Q_{38}	0.022651	0.000097	−0.022430	0.009080
$E_{s_M,s_M}(000)$	Q_{39}	1.499727	1.474196	1.222313	1.035356
$E_{s_M,s_M}(110)$	Q_{40}	−0.024254	−0.041598	−0.024446	−0.026552
$E_{s_M,x_M}(110)$	Q_{41}	−0.002273	−0.011439	−0.012007	−0.004485
$E_{x_M,x_M}(000)$	Q_{42}	1.572115	1.613293	1.632127	0.868113

Table 1. (*cont.*)

Name of energy integral used as parameter	Nomenclature used in computer program and in appendices A and B	Values for			
		TiN	ZrN	ScN	ScP
$E_{x_M,x_M}(110)$	Q_{43}	−0.009866	0.006063	0.020430	−0.001180
$E_{x_M,x_M}(011)$	Q_{44}	−0.031083	−0.050590	0.007057	−0.047543
$E_{x_M,y_M}(110)$	Q_{45}	0.041203	0.059331	0.065020	0.033465
Root mean square deviation (in mRyd)		10.4	10.2	9.3	9.4
Maximum deviation (in mRyd)		21.4	20.8	20.2	19.1

LCAO eigenvalues from the APW energies. In the first column the names of the energy integrals are given using the nomenclature of Refs. [5–9]. The second column contains the names of the parameters as used in Appendices A and B.

Generally speaking the maximum deviation of the interpolated from the *ab initio* energies lies about 0.02 Ryd which for most of the cases is noticeably smaller than in Ref. [7].

The LCAO energies should not only lie as close as possible to the APW energy states, they should also possess a similar l character. One way of checking this is to compare the LCAO partial densities of states [7] constructed from the LCAO eigenvectors with the APW character densities [4–7]. The principal features of these two sets of quantities prove indeed to be the same. Minor differences are due to the coarser $\boldsymbol{k}$ mesh of the APW calculation and to the fact that whereas the LCAO partial l-like densities of states are set up for the whole elementary cell, the APW character densities are defined only for a particular muffin tin sphere.

A comparison of the present LCAO interpolation using thirteen Bloch sums as basis with the nine Bloch sums interpolation of Ref. [7] shows a strong dependence of the values for the various parameters on the number of basis functions. The general aspect of the partial l-like densities of states is the same for both interpolations but there are some differences in the fine structure due to the different quality of the fits and to the fact that some of the missing functions in the old nine Bloch sums fit are simulated by other functions. The nine Bloch sums fit showed for example a non negligible non metallic s partial density of state in the energy region of the d bands. If metal s and p functions are included in the basis as in the present interpolation, this non metallic s component is replaced by a metallic s component of the density of states.

In the following paragraphs the fits are discussed in detail for every compound. To illustrate the discussion the plotted LCAO band structures using 333 non equivalent $\boldsymbol{k}$ points in the symmetry directions $\Gamma \rightarrow \Delta \rightarrow X \rightarrow Z \rightarrow W \rightarrow Q \rightarrow L \rightarrow \Lambda \rightarrow \Gamma \rightarrow \Sigma \rightarrow K$ are shown in Figs. 1 to 4. Little crosses mark the APW energies.

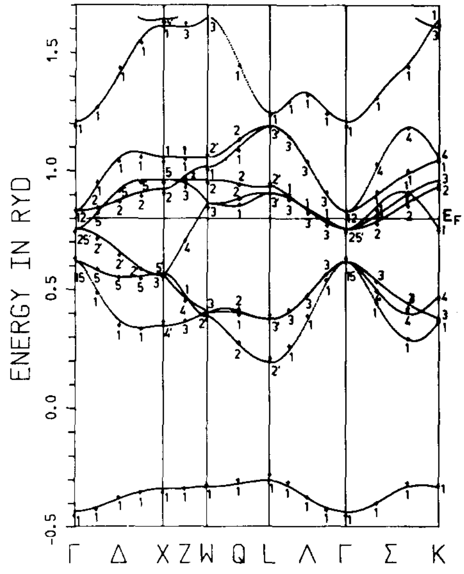

Fig. 1. Interpolated LCAO energy bands (points) and APW eigenvalues (shown as crosses) for TiN. E_F is the Fermi level. All energies are given with respect to the constant muffin-tin potential

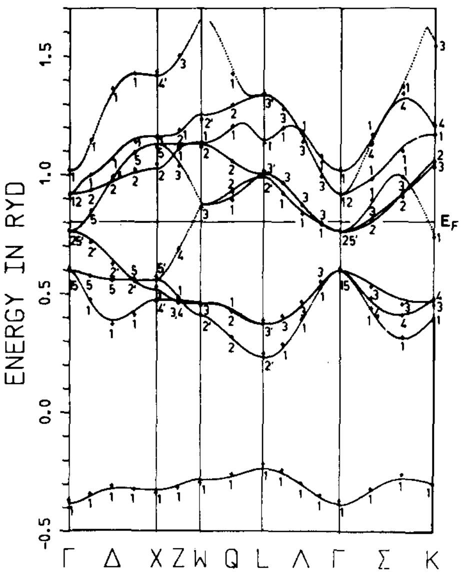

Fig. 2. Interpolated LACO energy bands (points) and APW eigenvalues (shown as crosses) for ZrN. E_F is the Fermi level. All energies are given with respect to the constant muffin-tin potential

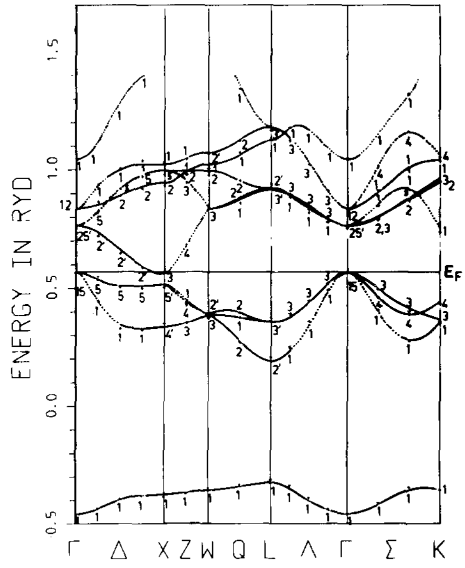

Fig. 3. Interpolated LCAO energy bands (points) and APW eigenvalues (shown as crosses) for ScN. E_F is the Fermi level. All energies are given with respect to the constant muffin-tin potential

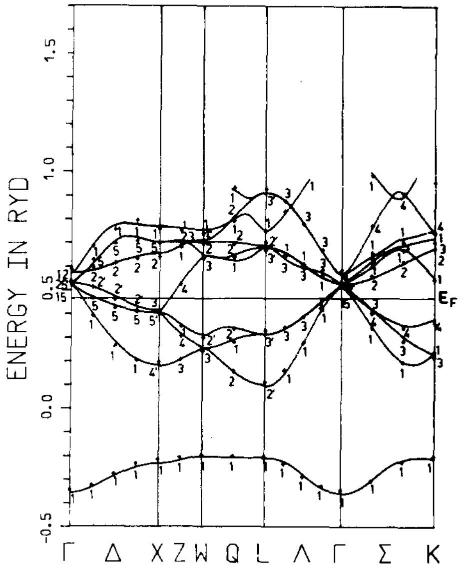

Fig. 4. Interpolated LCAO energy bands (points) and APW eigenvalues (shown as crosses) for ScP. E_F is the Fermi level. All energies are given with respect to the constant muffin-tin potential

1. TiN

As shown in Fig. 1 ten bands and parts of the eleventh band up to 1.65 Ryd (0.9 Ryd above the Fermi level) were satisfactorily fitted with a maximum deviation of 21.4 mRyd. Contrary to predictions in Ref. [7] that the LCAO method should not be suitable for fitting the higher unoccupied bands, all bands seem to be equally well fitted. The good fit of the tenth band was however only possible because the basis contained also Bloch sums originating from metal *p* functions. Whereas the tenth valence band of TiN has pure metal *s* character at the origin of the Brillouin zone (Γ), only an appropriate linear combination of metallic *p* functions $(p_x + p_y + p_z)$ is a suitable basis at the surface of the Brillouin zone (at the point $L = (444)\pi/4a$) for the irreducible representation L_1.

A comparison of the numerical values of the present LCAO parameters with those of Ref. [7] shows that most of the parameters have fairly different values—especially those describing interactions with non metal *p* functions. Probably these parameters include implicitely effects of metallic *p* functions in case of the previously used nine Bloch sums interpolation. Therefore most of the parameters besides the most important ones with similar values in both calculations are strongly basis dependent.

2. ZrN

As shown in Fig. 2 ten bands up to 1.65 Ryd (0.85 Ryd above the Fermi level) were fitted with a maximum deviation of 20.8 mRyd. Unfortunately the eleventh band beginning at 1.42 Ryd (0.65 Ryd above E_F) shows metallic *f* symmetry at Γ (irreducible representation $\Gamma_{2'}$) and metallic and non metallic *d* symmetry along the symmetry direction Δ ($\Delta_{2'}$). The present LCAO calculation cannot reproduce this part of the tenth band because the basis neither contains Bloch sums originating from metallic *f* nor from non metallic *d* functions.

3. ScP

An analysis of the APW partial *l*-like charges [5] for each eigenvalue of ScP reveals that in this case already the tenth band possesses a certain amount of phosphorous *d* character (mainly of t_{2g} symmetry at Δ, Σ, Λ, but also components of e_g symmetry for other states). As the LCAO basis does not contain Bloch sums formed from phosphorous *d* orbitals the fit is rather bad for parts of the tenth band. Therefore only nine bands plus the overlapping part of the tenth band including APW energies up to 0.85 Ryd (6.12 eV above the Fermi level) were fitted for ScP. In this limited energy range the maximum deviation of the fitted energy bands from the APW eigenvalues was only 19.1 mRyd.

Fig. 3 shows the LCAO band structure of ScP together with the APW energies marked as crosses.

4. ScN

Fig. 4 shows the LCAO band structure of ScN together with the APW energies marked as little crosses. Energies up to 1.4 Ryd (11.5 eV above the Fermi level) were fitted including in this case nine bands and parts of the tenth band. The maximum deviation was 20 mRyd.

4. Conclusion

The successful inclusion of four Bloch sums originating from transition metal *s* and *p* orbitals in the basis for the LCAO fit makes it possible to extend the energy range of the fit and to augment the number of valence bands to be fitted. Contrary to predictions in Ref. [7] all bands are equally well fitted if they do not possess a large component of transition metal *f* or non metal *d* character as for example the tenth valence band of ScP. In this case it would be advantageous to include additional Bloch sums arising from metallic *f* or non metallic *d* orbitals in the basis.

The additional inclusion of Bloch sums constructed from non metal *d* functions would change the dimension of the LCAO Hamiltonian matrix from 13 to 18 and the total number of different energy integrals from 45 to 74 taking into account interactions up to third-nearest neighbours. Besides demanding more computer time for the fit it would also be necessary to know APW or other first principles energy eigenvalues up to very high energies - at least for the most important symmetry points.

Whereas feasible with fast computers and the new symmetry-controlled version of the fitting program which enables us to use more or less arbitrary numbers as starting values for the LCAO parameters this extension would however make the LCAO fit more cumbersome - an aspect which should not be neglected at a moment where a number of fast band structure methods (LMTO, LAPW, fast KKR) are available.

Acknowledgements. The authors thank the "Interuniversitäres Rechenzentrum der Universität Wien" where all calculations were performed, for their friendly support. This work was supported by the Austrian "Fonds zur Förderung der wissenschaftlichen Forschung" (Project No. 2619), which is gratefully acknowledged.

Appendix A: Reduced Submatrices of the LCAO Hamiltonian Matrix for $k_j = W = (048)\pi/4a$ for a Compound with Rocksalt Structure

When using symmetry-adapted linear combinations of Bloch sums as basis, the 13×13 LCAO Hamiltonian matrix splits at the symmetry point W into a 1×1 submatrix belonging to the irreducible subspace of W_2, two degenerate 3×3 matrices for the irreducible subspaces W_3, a 3×3 submatrix for W_1 and finally another 3×3 matrix for $W_{2'}$. The matrix elements of these submatrices are given below including only interactions with next and second-nearest neighbours. The LCAO parameters Q_i are designated according to Table 1.

W_2: A Bloch sum originating from a metallic t_{2g} orbital is the basis.

$$[Q_{25}-4Q_{26}]$$

W_3: (twice degenerate)

The basis consists of Bloch sums formed from metallic and non metallic p functions and from a metallic t_{2g} orbital.

$$\left[\begin{array}{ccc} p_N & (t_{2g})_M & p_M \\ Q_{10}-4Q_{11} & 2iQ_{14} & 2Q_{21}-2Q_{22} \\ & Q_{25}-4Q_{27} & 4i(Q_{31}-Q_{32}) \\ & & Q_{42}-4Q_{43} \end{array}\right]$$

W_1: The basis contains Bloch sums formed from non metallic s and metallic p and e_g orbitals.

$$\left[\begin{array}{ccc} s_N & (e_g)_M & p_M \\ Q_1-4Q_2 & 2\sqrt{3}Q_5 & 2iQ_8 \\ & Q_{33}-4Q_{35} & -8iQ_{38} \\ & & Q_{42}-4Q_{44} \end{array}\right]$$

$W_{2'}$: The basis consists of Bloch sums constructed from non metallic p and metallic s and e_g orbitals.

$$\left[\begin{array}{ccc} p_N & (e_g)_M & s_M \\ Q_{10}-4Q_{12} & 2iQ_{17} & 2iQ_{19} \\ & Q_{33}-4Q_{34} & -4Q_{36} \\ & & Q_{39}-4Q_{40} \end{array}\right]$$

Appendix B: Correct Sequence of LCAO Eigenvalues at $k_j = W$ (an Example for Symmetry Control)

To set up the conditions for the correct sequence of LCAO eigenvalues at a special symmetry point (in this case W) Table 2 is constructed.

In its first column the names of all the irreducible representations of $\mathcal{G}_{k_j}$ with APW energies in the interesting energy range of the valence bands are tabulated. All these APW energies are numbered in increasing order of magnitude and these numbers listed in column 2. In brackets one finds the main l character of the energy state to which the eigenvalue belongs. In our example we treat the refractory compound TiN with a non metal s band followed by non metallic p, metallic d, metallic s and p bands.

Then the formulae for the diagonal matrix elements of the reduced Hamiltonian submatrices given in Appendix A are inspected for suitable parameters appearing only in one of these submatrices.

Table 2. Symmetry control for the k-point W of TiN

Irreducible representation μ	Number of APW eigenvalue (TiN)	Corresponding LCAO energy should depend on	$\frac{\partial E_n(k_j)}{\partial Q_j(\mu)}$
W_1	$1[s_N]$	Q_2	<0
	$6[(e_g)_M]$	Q_{35}	<0
	$10[p_M]$	Q_{44}	<0
W_3	$2[p_N]$	Q_{11}	<0
	$4[(t_{2g})_M]$	Q_{27}	<0
	$8[p_M]$	Q_{43}	<0
W_2	$5[(t_{2g})_M]$	Q_{26}	<0
$W_{2'}$	$3[p_N]$	Q_{12}	<0
	$7[(e_g)_M]$	Q_{34}	<0
	$9[s_M]$	Q_{40}	<0

These parameters are written down in the third column of the table. The fourth column contains information about the sign of the energy derivative $\partial E/\partial Q_j$.

Of course every eigenvalue of the submatrix for the irreducible space W_1 would depend on the parameter Q_2 (second nearest neighbour interaction between two non metal s orbitals) but this dependence will be strongest for the eigenvalue belonging to the non metal s band i.e. the first eigenvalue for TiN.

The program asks therefore if the smallest LCAO eigenvalue decreases with increasing Q_2. If not, the next LCAO eigenvalue depending on Q_2 is searched for and interchanged with the first LCAO eigenvalue. For TiN the second energy should be the smallest energy for the irreducible representation W_3 belonging to the non metallic p band. With our table we find that it should depend on Q_{11}. If the second LCAO eigenvalue does not decrease with increasing Q_{11}, the smallest energy fulfilling this condition is interchanged with $E_2(\boldsymbol{k}_j)\ldots$ and so on until the sequence of LCAO energies equals the sequence of APW eigenvalues for $\boldsymbol{k}_j = W$ and all the other symmetry points and directions.

This method works satisfactorily for the simple band structures treated in this paper. For more complicated band structures it might be necessary to use a sharper criterion.

Instead of asking only if for example

$$\frac{\partial E_1(\boldsymbol{k}_j)}{\partial Q_2} < 0$$

one asks if

$$\frac{\partial E_1(\boldsymbol{k}_j)}{\partial Q_2} < 0 \qquad \text{and} \qquad \left|\frac{\partial E_1(\boldsymbol{k}_j)}{\partial Q_2}\right| = \max \left|\frac{\partial E_n(\boldsymbol{k}_j)}{\partial Q_2}\right| \; n = 1 \cdots 13$$

and finds out which of the LCAO eigenvalues shows the strongest dependence on Q_2. If necessary this eigenvalue is then interchanged with the first energy.

References

1. Schlegel, A., Wachter, P., Nickl, J. J., Lingg, H.: J. Phys. C.: Sol. State Phys. **10**, 4889 (1977)
2. Schlegel, A.: Thesis: ETH Zürich (1979)
3. Ehrenreich, H., Cohen, M. M.: Phys. Rev. **115**, 786 (1959)
4. Podloucky, R.: private communication
5. Wimmer, E., Neckel, A., Schwarz, K., Eibler, R.: J. Phys. C.: Sol. State Phys. **12**, 5453 (1979)
6. Ripplinger, H.: Diplomarbeit, TU Wien (1976); Schwarz, K., Ripplinger, H., Neckel, A.: in preparation
7. Neckel, A., Rastl, P., Eibler, R., Weinberger, P., Schwarz, K.: J. Phys. C.: Sol. State Phys. **9**, 579 (1976)
8. Slater, J. C., Koster, G. F.: Phys. Rev. **94**, 1498 (1954)
9. Connolly, W. D.: Proc. 3rd I.M.R. Symposium: Electronic Density of States, NBS Spec. Publ. **323**, 27 (1971)
10. Löwdin, P.-O.: Adv. Phys. **V**, 3 (1956)
11. Schwarz, K.: Mh. Chemie **102**, 1400 (1971)
12. Mattheiss, L. F.: Phys. Rev. **B5**, 290 (1972)
13. Honig, J. M., Wahnsiedler, W. E., Dimnock, J. O.: J. Sol. State Chem. **5**, 452 (1972)
14. For example: Pilar, L. F.: Elementary quantum chemistry: New York: McGraw-Hill Book Company 1968
15. Dorrer, M., Eibler, R., Neckel, A.: in preparation
16. In preparation

Received March 31/August 19, 1981