Trends in bulk electron-structural features of rocksalt early transition-metal carbides

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Abstract

A detailed and systematic density-functional theory (DFT) study of a series of early transition-metal carbides (TMCs) in the NaCl structure is presented. The focus is on the trends in the electronic structure and nature of bonding, which are essential for the understanding of the reactivity of TMCs. The employed approach is based on a thorough complementary analysis of the electron density differences, the density of states (DOS), the band structure and the real-space wavefunctions to gain an insight into the bonding of this class of materials and get a more detailed picture of it than previously achieved, as the trend study allows for a systematic identification of the bond character along the different bands. Our approach confirms the presence of both the well-known TM–C and TM–TM bonds and, more importantly, it shows the existence and significance of direct C–C bonds in all investigated TMCs, which are frequently neglected but have been identified in some cases (Zhang et al 2002 Solid State Commun. 121 411; Ruberto et al 2007 Phys. Rev. B 75 235438). New information on the spatial extent of the bonds, their k-space location within the band structure and their importance for the bulk cohesion is provided. Trends in covalency and ionicity are presented. The resulting electron-structural trends are analyzed and discussed within a two-level model.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

An extensive study of the reactivity of the transition-metal carbide and nitride (TMX) surfaces is being performed with density-functional theory (DFT) [1–6]. It is aimed at an understanding of reactivity from fundamental principles, similar to the one available today for pure metal surfaces [7]. Due to the intimate relation between bulk and surface electronic structures, a careful mapping of trends in the bulk electronic structure is essential for the overall purpose to understand the trends in reactivity of the transition-metal carbides (TMCs). Therefore, a bulk background focusing on the trends in electronic structure and the nature of bonding in the early TMCs is provided here.

The relevance of the results is, however, broader, as the bulk TMXs are also interesting by themselves, having such properties as extremely high melting point, ultrahardness and metallic conductivity [8, 9]. As a consequence, the importance of the electronic structure trends for atomic structure and stability is also analyzed.

The bulk TMXs have been studied experimentally and theoretically with a large number of techniques [1, 10–19, 21–25]. Already the early studies agree on the fact that the bonding in these compounds involves simultaneous contributions from metallic, covalent and ionic bonding [11]. The main electronic structure properties are related to (i) the direction and amount of charge transfer between the TM and X atoms, responsible for the ionicity of the material, and (ii) the modifying effect on the metal d band upon carbide/nitride formation, responsible for the formation of hybridized bonding and antibonding pd states. The decreasing stability of the TMCs in the NaCl structure from left to right along a period in the periodic table has been explained as arising from the successive filling of the antibonding TM d–C p states in a rigid-band model [13, 15, 21].

The contributions to the cohesive energy from the TM–C, TM–TM and C–C bonds, respectively, have been approximately determined quantitatively by a two-sublattice model of the NaCl structure based on DFT calculations [14]. These results confirm the dominance of the TM–C bond
subgroup of TMCs (figure 1) is carefully chosen to allow a obtained knowledge of the electronic structure. The studied compared with earlier studies and analyzed on the basis of the space wavefunctions. Key bulk properties are calculated, way to obtain detailed information on the bond character: electronic structure analysis tools are employed in a joined number of non-magnetic early TMCs. Complementary from the calculated electronic structures.

Our systematic DFT investigation is performed on a number of non-magnetic early TMCs. Complementary electronic structure analysis tools are employed in a joined way to obtain detailed information on the bond character: valence-electron density differences, Bader charge analyses, band structures, projected densities of states (DOSs) and real-space wavefunctions. Key bulk properties are calculated, compared with earlier studies and analyzed on the basis of the obtained knowledge of the electronic structure. The studied subgroup of TMCs (figure 1) is carefully chosen to allow a monitoring of trends with respect to the constituent transition metal (TM) along both the period and group within the periodic table. Our aim is to describe variations both along and between the 3d, 4d and 5d TM series and we have therefore chosen TMs from each period, for which TMCs in the rocksalt structure have been observed in stable or metastable phases. Also, some of these TMCs are widely used in applications. We argue that the subgroup is large enough to pick up the important trends.

Many TMCs crystallize in the sodium chloride structure, either as stable, including ScC (at normal pressures), TiC, VC, ZrC, NbC and TaC, or metastable compounds, such as δ-MoC and WC. The choice of the TMCs in the NaCl structure is natural for our calculations since the number of varying parameters should be kept small when performing a trend study to allow for an identification of the important electronic factors. Because of this, CrC, which to our knowledge has not been observed in CrC stoichiometry, is not included in our investigation. On the other hand, although in some definitions the group III metals are not considered to be transition metals, we include ScC, which crystallizes in the rocksalt structure, to widen the scope of our trend study.

This paper is organized as follows. First, the computational details are summarized in section 2. Then, in section 3, the results from our calculations are presented and the obtained trends analyzed, including atomic geometry and stability (section 3.1), electron density and charge transfer (section 3.2), and detailed electronic structure (section 3.3). In section 4, these trends and the nature of bonding in the TMCs are summarized, discussed and related. The main conclusions of our study are summarized in section 5.

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**Figure 1.** The early transition-metal carbides under investigation, organized according to their parent-metal position in the periodic table.

Table 1. Calculated lattice parameters ($a_0$), cohesive energies ($E_{coh}$), bulk moduli ($B_0$) and Bader charge transfers from TM to C atoms (Bader). The corresponding experimental values are given in parentheses. The calculated $E_{coh}$ values are defined by equation (1).

| TMC  | $a_0$ (Å)    | $E_{coh}$ (eV/unit cell) | $B_0$ (GPa) | Bader (|e|/atom) |
|------|-------------|-------------------------|-----------|---------------|
| ScC  | 4.684 (4.637$^a$) | 12.39 (12.74)$^b$ | 148 (—) | 1.54          |
| TiC  | 4.332 (4.325$^c$) | 14.90 (14.32)$^d$ | 242 (232–390)$^f$ | 1.49          |
| VC   | 4.164 (4.163$^e$) | 13.88 (13.88)$^d$ | 290 (308–390)$^d$ | 1.41          |
| ZrC  | 4.702 (4.691$^e$) | 15.93 (15.86)$^d$ | 258 (159–224)$^d$ | 1.70          |
| NbC  | 4.492 (4.454$^e$) | 15.83 (16.52)$^f$ | 293 (296–330)$^d$ | 1.64          |
| TaC  | 4.450 (4.270$^f$) | 13.11 (14.45)$^f$ | 319 (—) | 1.97          |
| MoC  | 4.479 (4.453$^f$) | 17.34 (17.12)$^f$ | 321 (214–414)$^d$ | 1.94          |
| WC   | 4.382 (4.392$^f$) | 15.67 (16.49)$^f$ | 357 (—) | 1.60          |

$^a$ Reference [25]. $^b$ Reference [17]. $^c$ Reference [33].
$^d$ References [9, 24]. $^e$ Reference [18]. $^f$ Reference [19].
$^g$ Reference [20].

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2. Computational details

The calculations presented in this paper are performed within the well-established DFT formalism using the plane-wave pseudopotential code Dacapo [26]. The ion–electron interaction is treated with Vanderbilt ultrasoft pseudopotentials [27]. The exchange–correlation energy is included by the generalized gradient approximation (GGA), using the PW91 functional [28]. All the bulk calculations are performed with a Monkhorst–Pack sampling [29] of $8 \times 8 \times 8$ special $k$-points and a cutoff energy for the plane-wave expansion of 400 eV. The similarities and differences in the nature of bonding in the considered TMCs are studied with the following electronic structure analysis tools: electronic density differences, Bader charge analyses [31, 32], band structure diagrams, atom-projected local DOSs and Kohn–Sham wavefunctions. The Bader analysis is a charge-localization analysis that is able to give quantitative information on the electron localization around different ions. The scheme used here is based on the approach described in [31, 32].

3. Results and analysis

3.1. Geometry and stability

In table 1 and figure 2 we present the calculated lattice parameters, bulk moduli and cohesive energies, together with the available experimental data. The lattice parameters and the bulk moduli are obtained with a Murnaghan equation of state [30] and the cohesive energies are calculated as

$$E_{coh} = E_{solid} - \sum_{\text{atoms}} E_{isolated}.$$  (1)

There is good agreement between calculated and experimental values. For the lattice parameters the deviations are smaller than 1%. Our calculated lattice constants are also in quantitative agreement with other published theoretical results, obtained with both the PW91 and the RPBE GGA functionals [24].
Figure 2. Variations of, from left to right, the lattice parameters, the cohesive energies and the bulk moduli of the investigated 3d, 4d and 5d TMCs as a function of the group number of their parent transition metals.

Figure 3. The linear correlations of the TMC lattice parameters with the covalent radii [35] (squares) and with the ionic radii [36] (circles) of the parent transition metals.

For both the cohesive energies and the bulk moduli the deviations from experiments are larger. Still, our results agree well with other theoretical values [23–25]. The deviations from experiments can be understood from the fact that, in reality, the TMCs often occur as substoichiometric phases, with strongly varying amounts of carbon vacancies. It is known that several bulk properties depend strongly on such defects [22, 34].

The trends in lattice parameters can be understood qualitatively by plotting them against empirical covalent [35] and ionic [36] radii (figure 3). The overall linear correlations indicate that the bonding in the TMCs contains both covalent and ionic effects. This iono-covalent mixture agrees with earlier studies [11] and is examined in more detail in our analysis of the electronic structure below.

The cohesive energies increase monotonically down a group in the periodic table. Along each period, they exhibit a maximum for group IV. These trends are compatible with the experimental values (see table 1) if the experimental error bars, which are ~±0.4 eV/unit cell (see estimates of the uncertainty in [17–19]), are taken into account. As will be argued below, the trends in the cohesive energies can be understood from the trends of the bulk electronic structure.

3.2. Valence-electron density and charge transfer

Three-dimensional contour plots of the differences between the valence-electron densities in the bulk TMCs and the electron densities of free TM and C atoms are shown in figure 4 for the considered TMCs. The changes in the distribution of the valence electrons upon bond creation in the bulk TMCs reveal (i) a partially ionic character of the bond, seen as quite localized electron clouds (orange–red regions) around the C atoms, indicating a charge transfer from TM to C, and (ii) covalent TM–C σ bonds, seen as a localization of charge (orange) in the region in between the TM and C atoms.

Our Bader analysis results presented in table 1 confirm that the TMCs are partly ionic compounds. Charge is transferred from TM to C for all considered compounds, as expected from the higher electronegativity of C. This direction of the charge transfer is confirmed experimentally by the near-edge x-ray absorption fine structure (NEXAFS) technique [37].

The covalent nature of the bonding is most evident in TiC and VC, as shown by the charge-difference contours (figure 4) and by the lower Bader charge transfer for these compounds. In general, the Bader charge trends indicate (i) an increase in covalency and a decrease in ionicity (an exception is the metastable δ-MoC), when moving from left to right along a period, and (ii) a decrease in covalency and an increase in ionicity down a group.

All of the considered carbides except MoC and WC are stable in the NaCl structure. The electron density difference alone cannot explain why this is the case. To gain an understanding of the structural change of WC other methods must be employed, including the ones in section 3.3.

3.3. Electronic structure and nature of bonding

3.3.1. General features. Calculated total and atom-projected DOSs and band structures for the considered bulk TMCs are shown in figures 5 and 6, respectively. Furthermore, complementary information about the bond character for different bands and k-points is obtained by investigating the real-space Kohn–Sham wavefunctions in detail. Such an analysis is performed for all the TMCs. The results are presented in figure 6 and a representative selection of the different bond types is illustrated in figure 7.
The contribution to the bonding from the LVB is presumably small due to the small hybridization of the TM and C states. Points (ii) and (iii) illustrate the presence of a covalent bond. The mainly C 2p and TM d characters of the UVB and CB, respectively, indicate a charge transfer from the TM d orbitals to the C 2p orbitals and thus a partially ionic bonding nature (cf pages 189–90 in [38]). This is supported by our calculated Bader charges, given in table 1. Orbital-projected DOSs show that the TM states are of predominantly $e_\text{g}$ and $t_{2g}$ symmetry in the UVB and in the CB, respectively. Property (iv) explains the metallic character of the TMCs.

An analysis of the Kohn–Sham wavefunctions along the $k$-symmetry lines of figure 6 shows that the band structure is dominated by TM–C states (see figures 7(a) and (b) for representative TM–C bonds in the case of VC). These states are found throughout the whole energy region of the $k$-space, that is, they are present in both the LVB and the UVB, as well as in the CB.

The wavefunction analysis reveals also that large parts of the states in the LVB and in the lower energy range of the UVB have a bonding C–C character of both $\sigma$ and $\pi$ symmetry (see figures 7(d)–(e) for representative C–C bonds in the case of bulk VC).

Finally, TM–TM states are evident in significant parts of both the UVB and the CB (see figure 7(c) for a representative TM–TM bond in the VC system). In all the TMCs, at least one band of TM–TM character crosses $E_F$.

The wavefunction analysis confirms also the picture that the UVB states have a bonding symmetry, while the CB states show a more antibonding character (i.e. nodes in between the atoms).

Experiments on the band structures for single bulk crystals of group IV–VI TMCs have been carried out by using, for example, angle-resolved photoemission spectroscopy (ARPES), in particular x-ray photoemission spectroscopy (XPS) for the mapping of occupied bands and inverse photoemission spectroscopy (IPES) for the mapping of unoccupied bands (see [22] and references therein). These results agree with the rough features of our calculated results but do not provide any information on the different bond characters of the different bands, which our method is able to give.

### 3.3.2. Trends along a period.

The DOS figures, together with the band structure and wavefunction analyses, show that, as the TM group number increases, (i) both the UVB and the CB (as well as the LVB) are shifted down in energy relative to $E_F$, due to the filling of bands; (ii) as a consequence the metallicity (i.e. the number of states at $E_F$) increases; (iii) the bands crossing $E_F$ show more TM–TM character; (iv) the energy separation between the UVB and the CB decreases; (v) the UVB becomes less C localized; and (vi) the overall amount of C–C states decreases.

### 3.3.3. Trends along a group.

As the TM period number increases the following general features are observed in the DOS, band structure and wavefunction plots: (i) the position of $E_F$ relative to the center of mass of the UVB and the CB is unchanged; (ii) the bond character of the different states.

![Figure 4. Valence-electron density difference for the bulk systems, compared to the free constituent TM and C atoms. For each system, 20 isosurfaces homogeneously distributed in the interval $[-0.4, 0.5]$ electrons Å$^{-3}$ are shown. The color coding is blue (reduction of electron density) through yellow (no density difference) to red (increase in electron density). An isosurface with a given value has the same color coding in all systems. Larger (smaller) balls correspond to TM (C) atoms. The atom in the central red region is C. The orange isosurface (+0.185 electrons Å$^{-3}$) located in between TM and C atoms shows the directional covalent TM–C bond and is most pronounced and directional for TiC and VC. The overall electronic structure is similar for all considered TMCs and is characterized by (i) a deeply bound lower valence band (LVB) with C 2s states and a very small amount of TM d states; (ii) a filled (or, for ScC, partly filled) bonding upper valence band (UVB) below the Fermi level ($E_F$), with overlapping C 2p and TM d states; (iii) an empty or partly filled antibonding conduction band (CB) above or around $E_F$, dominated by TM d states with a clear contribution from C 2p states; and (iv) a non-vanishing DOS in the pseudogap between the UVB and the CB.](image-url)
is largely unchanged; (iii) the energy separation between the UVB and the CB increases; and (iv) the UVB becomes more C localized. The differences between periods 5 and 6 are smaller than the differences between periods 4 and 5.

Also, a detailed investigation of the band structure reveals that the energetical order of the bands changes: (i) at the $\Gamma$-point the higher TM–TM band moves up in energy, while TM–C bands move down; and (ii) the two lowest UVB bands at the...
Figure 6. Calculated band structures for the considered TMCs. The parts of the bands that correspond to TM–TM, TM–C and C–C bonding states, respectively, are indicated. The identification of the bond character is based on the Kohn–Sham wavefunctions as described in the text and visualized in figure 7.
Figure 7. Three-dimensional real-space contour plots of a representative selection of the Kohn–Sham wavefunctions $|\Psi_{nk}(r)|$ in bulk VC illustrating the different types of bonds at specific $k$-points and bands $n$ (here, $n = 1$ corresponds to the lowest valence band, cf figure 6): (a) TM eg–C $p\sigma$ bonds found in the lowest UVB band ($n = 2$) between $\Gamma$ and $X$, (b) TM t$_{2g}$–C $p\pi$ bonds at $L_{n=3}$, (c) TM t$_{2g}$–TM t$_{2g}$ $\sigma$ at $X_{n=3}$, (d) C–C $p\sigma$ at $W_{n=2}$, (e) C–C $p\pi$ at $L_{n=2}$ (there is no connection to the V atoms). The given contour plots are for the same value of $|\Psi_{nk}(r)| = 0.30$. Larger (gray) balls correspond to V atoms and smaller (black) balls to C atoms.

X-point (the C–C and the TM–TM bands) approach each other and change places.

3.4. Understanding the trends

In a simple model, the above trends could be understood on the basis of a two-level system, comprised of the valence d and p states of the free TM and C atoms, respectively (see figure 8). This discussion resembles the one for a heteronuclear diatomic molecule (see, for example, [38]). Due to the lower electronegativity of the TM atom, the energy of the TM d state is higher than that of the C p state. Their interaction results in bonding $E_b$ and antibonding $E_a$ states, the UVB and the CB, respectively, separated by an energy $W$ (see figure 8). Assuming a one-electron picture, the solutions to the Schrödinger equation are

$$E_b = \varepsilon - \sqrt{\Delta^2 + \beta^2},$$

$$E_a = \varepsilon + \sqrt{\Delta^2 + \beta^2},$$

with $\varepsilon = (E_{TM} + E_C)/2$ and $\Delta = (E_{TM} - E_C)/2$, where $E_{TM}$ is the energy of the TM d level and $E_C$ is the energy of the C p level, and $\beta = \langle C|H_{12}|TM \rangle$. If $\Delta \neq 0$, which is the case here, there is a charge transfer from TM to C and the bond is partially ionic.

As the TM d-electron subshell becomes full, the TM d level is shifted down in energy, giving a better energy overlap between the TM and C states. This results in a stronger pd hybridization, a smaller $\Delta$ and a bond of more covalent character, that is, a more similar amount of TM and C localization of the UVB. At the same time, the increase of
the number of valence electrons causes a shift of $E_F$ towards higher energies. From equations (2) and (3), the separation between UVB and CB is given by

$$W = 2(\Delta^2 + \beta^2)^{1/2}.$$  \hspace{1cm} (4)

Such a model works well for our considered TMCs based on TMs in period 4 (Sc, Ti and V). Since each extra valence electron is added in the 3d subshell, one can assume to a first approximation that $\beta$ is constant for our period 4 TMCs. The values of $W$ can be estimated from our calculated DOSs and the values of $\Delta$ can be obtained from the all-electron calculations performed when generating the pseudopotentials used in our DFT calculations. In figure 9, a plot of $W^2$ versus $\Delta^2$ shows a linear relationship with gradient equal to 4, in excellent agreement with equation (4). The monotonic decrease of $W$ as the number of TM 3d electrons increases also agrees well with the decrease in ionicity along period 4 shown by our calculated Bader values.

However, such a simple model fails when describing our period 5 TMCs, as shown in figure 9. The reason for this can be found in the fact that Nb and Mo form exceptions to the common electron-filling rule, as they only have half-filled 5s subshells. The d level energy of Nb (as obtained from the all-electron calculations) is therefore higher than that of Zr. Hence, there is not a monotonic downshift of the TM d level energy along the period. In order to explain the monotonic variations of $W$ observed in our DOS calculations either a modification of the atomic energy levels, for example, through intra-atomic hybridization, or an extension of the model to include additional levels, for example, the TM s level, seems therefore to be necessary.

Moving down a group, the number of valence electrons is constant, leaving $E_F$ at the same energy. In addition, the value of $\beta$ can be expected to increase, due to the increase of the geometrical extent of the valence orbitals. Within the two-level model, this contributes to an increase in $W$, as observed in our calculated DOSs.

4. Discussion

In this paper we present a systematic and detailed trend study of the electronic structure of a collection of early transition-metal carbides based on DFT calculations.

The results confirm the mixed ionic-covalent TM–C and the metallic TM–TM nature of the bond. This is shown both by local DOS analyses and by a thorough analysis of the band structures and Kohn–Sham wavefunctions along several symmetry lines in the Brillouin zone (figure 6). TM–C bands are present throughout the whole energy range of the $k$-space, including the pseudogap between the UVB and the CB. Also, both a bonding and an antibonding TM–TM band are identified.

In addition, our analysis shows that in all the considered TMCs there exist direct C–C bonds, localized mainly in the lower part of the UVB. This presence is most pronounced in ScC (where C–C bands cross $E_F$) and decreases as the TM group and period numbers increase. The C–C bonds are also found in the pseudogap.

Figure 9. Correlation between the $W^2$ and $\Delta^2$ values, as defined in equation (4), extracted from our calculations for 3d and 4d TMCs. A linear fit is shown for each period. According to the two-level model for the bonding in the TMCs described in section 3.4 the correlation should be $W^2 = 4\Delta^2 + 4\beta^2$.

Hence, the C atoms play two roles for the bonding in the TMCs, by their interaction with the TM atoms and with other C atoms, respectively.

The valence-electron density difference analysis shows that the dominating bond character is the ionic-covalent TM–C bond, which is supported by the mapping of bands in the band structure (see figure 6). The trends in the covalent and ionic contributions can be extracted even though these two bonding types are closely intertwined. We find that the covalent contribution increases from left to right along a period and decreases down a group, while the ionic one decreases from left to right and increases down a group. In addition, our results show that there is a correlation between the covalency and the separation between the UVB and CB. A larger covalency corresponds to a smaller separation.

Although the TM–TM and C–C bonds are not observed in the density difference plots, their existence is revealed by the real-space wavefunction analysis. A contribution from C–C bonds to the TMC cohesion has been suggested in [14] based on a two-sublattice model. However, such a model does not take into account the modifying effect of the TM d states on the C orbitals in the C sublattice, and vice versa. Our approach identifies the different bonding types directly from the calculated electronic structure and therefore includes this modifying effect. We find that a significant amount of C–C states are present in all the studied TMCs, that is, not only the metastable ones, as was suggested in [14].

All the studied TMCs have a metallic bond character, that is, a non-vanishing DOS at $E_F$. These states (figure 6) are of both TM–TM and TM–C character (for ScC also C–C states). Indeed, measurements show that groups IV and V TMCs are almost as good electrical conductors as the parent metals [9]. With an increasing DOS at $E_F$ (figure 5), and assuming everything else is weakly varying, the conductivity should increase from group IV to group VI, which agrees with
measurements [9]. From the same arguments, the conductivity of ScC should be comparable to that of VC.

As discussed in section 3.1, along a period the calculated cohesive energies exhibit a maximum for group IV. The calculated electronic structure shows that, for group IV, $E_F$ is positioned in the pseudogap between the UVB and the CB, meaning that all the bonding UVB states are filled and all the antibonding CB states are empty. The same arguments as in the case of the bonding energy in a diatomic molecule can be applied, that is, a filling of bonding states increases the bond strength, while filling of antibonding states reduces the bond strength [10–12, 15, 21]. For ScC, not all bonding UVB states are filled and therefore the cohesive energy is lower for this compound. For groups V and VI, the antibonding CB states are partly filled, which again results in a weaker bond.

Down a group, the cohesive energies of the TMCs increase. This is because the UVB is shifted down in energy, making the bond stronger, while the CB is shifted up in energy, resulting in an energy gain due to the emptying of antibonding states.

It is interesting to note that the contribution from the metallic TM–TM states to the overall bonding follows similar trends, see figure 6. For group III, the TM–TM bands lie above $E_F$ and are thus unoccupied. For group IV, the bonding TM–TM bands cross $E_F$ and are thus partly filled. For group V, the bonding TM–TM bands are fully occupied. For group VI, the antibonding TM–TM bands in the CB are partly filled. The contribution to the overall bonding from the metallic TM–TM states is thus strongest for group V and weakens successively to the right and to the left of group V. In addition, the above-described upshift in energy of the CB down a group causes the occupation of the antibonding TM–TM states to be slightly lower in WC than in $\delta$-MoC. Therefore, among all the considered TMCs, the bonding contribution from the TM–TM states should be lowest for ScC and for $\delta$-MoC.

The band structure and Kohn–Sham wavefunction analyses show the origin of the instability of MoC and WC in the NaCl structure. The instability arises from the filling of antibonding states, as shown in figure 6. In MoC, the TM–TM antibonding band around $\Gamma$ is partly filled. In WC, two additional antibonding bands, of W–C character, cross $E_F$ around the $\Gamma$-point and become partly occupied. This picture agrees with previous studies [13] but also provides additional details.

The detailed analysis of the electronic structure provided in this study lays the essential foundation for the understanding of the TMCs’ surface properties, such as their surface reactivity. The surface characteristics of a material are tightly bound to its underlying bulk properties and will, of course, depend strongly on the type of bonds that are broken upon creation of the surface. It is known, for example, that the surface electronic structure of the TMC(100) surfaces is similar to that of the bulk. However, the TMC(111) surface shows both TM-localized as well as C-localized surface resonances [1, 5, 6]. The importance of these resonances on the surface reactivity is investigated in [5, 6].

5. Conclusions

This trend study deals with the bonding nature of early TMCs. Our approach is based on a complementary use of different types of electronic structure analysis tools. In particular, a thorough mapping of the band structure provides detailed insight into the bonding of the bulk TMCs. The results (i) confirm that the dominant contribution to the bond is the ionic-covalent TM–C bond, (ii) show the existence of TM–TM bonds and, importantly, (iii) reveal the existence of direct C–C bonds (most pronounced for ScC). We provide new information on the spatial extent of the different bonds, on their $k$-space location within the band structure, and on their importance for the bulk cohesion. Also, trends in covalency versus ionicity are obtained. The resulting electronic structural trends are analyzed and discussed within a two-level model.

These results are of importance for the understanding of the TMC surface reactivities, due to the intimate relation between bulk and surface electronic structures. When creating a surface by cutting a crystal, the breaking of TM–C, TM–TM and C–C bonds can manifest themselves as surface resonances and/or surface states at the surface. As we show in another study, not only TM but also C resonances play a crucial role in the bonding mechanism on TMC surfaces [5, 6].

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