

Effect of Valence Electron Concentration on Elastic Properties of 4d Transition Metal Carbides MC (M = Y, Zr, Nb, and Rh)

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The electronic structure and elastic properties of the 4d transition metal carbides MC (M = Y, Zr, Nb, Rh) were studied by means of extended Hückel tight-binding band electronic structure calculations. As the valence electron population of M increases, the bulk modulus of the MC compounds in the rocksalt structure does not increase monotonically. The dominant covalent bonding in these compounds is found to be M-C bonding, which mainly arises from the interaction between M 4d and C 2p orbitals. The bonding characteristics between M and C atoms affecting the variation of the bulk modulus can be understood on the basis of their electronic structure. The increasing bulk modulus from YC to NbC is associated with stronger interactions between M 4d and C 2p orbitals and the successive filling of M 4d-C 2p bonding states. The decreased bulk modulus for RhC is related to the partial occupation of Rh-C antibonding states.

Key Words : Electronic structure, Elastic properties, Transition metal carbides

Introduction

Refractory transition metal carbides (MC) are of particular interest, because they have an unusual combination of ceramic and metallic properties: high hardness, high temperature stability, good electrical and thermal conduction. Many of them crystallize in the rocksalt structure and are fairly simple to treat theoretically. These materials have been extensively studied over many years, both experimentally and theoretically.¹⁻¹⁶ The bonding features that have been clarified in these studies are useful in interpreting their physical properties. The common viewpoint is that covalent bonds can be formed between both metal-carbon and metal-metal pairs of atoms. At the same time, a transfer of electrons from M to C takes place, implying a certain degree of ionic bonding. We stress the importance of covalent metal-carbon bonds in explaining the stability and observed mechanical properties of these compounds. These properties are understood to arise in large part from strong covalent bonding between transition metal d and carbon p orbitals.

In this paper, we present the results of the electronic structures calculated for the carbides of 4d transition metals Y, Zr, Nb, and Rh. The presence of covalent M-C bonds and metallic M-M bonds is confirmed and analyzed in detail. In addition, the number of valence d electrons in the metals induces changes in bonding and elasticity in these compounds. It is, therefore, our goal to understand the relationship between the M-C bond strength and elastic properties of 4d transition metal carbides (MC) in the rocksalt structure as a function of the valence electron concentration (VEC) per atom, which is the total number of valence electrons in the structure divided by the number of atoms in a unit cell. As the VEC increases, the bulk modulus (B) increases from YC to NbC, and then decreases for RhC. This variation of B

with the number of metal d electrons can be explained as arising from the orbital mixing between metal and carbon and the successive filling of the consequent bonding and antibonding M 4d-C 2p states. The focus is on the trends in the electronic structure and the nature of bonding, which are essential for the understanding of the elastic properties of the transition metal carbides.

Our approach is based on a thorough complementary analysis of the density of states (DOS) and crystal orbital overlap population (COOP) to gain more profound insight into the bonding of this class of materials and get more detailed information on the bonding character than previously achieved. The COOP curves are indicative of the nature and strength of the bonding between a given pair of atoms, with positive and negative regions indicating bonding and antibonding states, respectively. The chemical bonding of M-C and M-M is quantitatively discussed by use of the bond overlap population based on supercell band structure calculations.

Computational Details

The tight-binding scheme based on the extended Hückel method^{17,18} is used to obtain the electronic structure of the 4d transition metal carbides. The atomic parameters used for our calculations are given in Table 1. We choose computational unit cells. The lattice sites of the crystal MC are generated by translation of the computational unit cells along three repeat vectors. The number of atoms in computational unit cell is four times larger than the basic unit cell (two atoms in the face-centered basic unit cell). Therefore, a supercell of four M and four C atoms is used to produce the projected DOS curves of Figure 1. The k-point meshes employed in the calculations are 512 k points in the Brillouin zone.

Table 1. Parameters for EH calculations

Atom	Orbital	H_{ii} , eV	ζ_1^b	ζ_2^b	c_1^a	c_2^a
Y	4d	-6.80	1.56	3.55	0.8316	0.3041
	5s	-7.02	1.74			
	5p	-4.40	1.70			
Zr	4d	-10.2	3.835	1.505	0.6210	0.5769
	5s	-8.0	1.817			
	5p	-5.4	1.776			
Nb	4d	-12.10	4.08	1.64	0.6401	0.5516
	5s	-10.10	1.89			
	5p	-6.86	1.85			
Rh	4d	-12.50	4.29	1.97	0.5807	0.5685
	5s	-8.09	2.135			
	5p	-4.57	2.100			
C	2s	-21.4	1.625			
	2p	-11.4	1.625			

^aCoefficients used in double- ζ expansion. ^bSlater-type orbital exponents.

Results and Discussion

Structural and Elastic Properties. The structural and elastic properties of 4d transition metal carbides have been studied by Korir *et al.*¹⁹ through *ab initio* calculations. Table 2 shows the values of the lattice constants and bulk moduli of MC (M = Y, Zr, Nb, and Rh) phases in the rocksalt structure (Fm-3m, No. 225) where the conventional unit cell contains four formula units with the transition metal atoms at Wyckoff site 4a (0, 0, 0) and carbon atoms at 4b (1/2, 1/2, 1/2).

It is observed from Table 2 that the bulk modulus becomes

Table 2. Calculated lattice constants (a_o) and bulk moduli (B) for 4d transition metal carbides MC (M = Y, Zr, Nb, Rh) in the rocksalt structure

	YC	ZrC	NbC	RhC
a_o (Å)	5.09	4.71	4.49	4.36
B (GPa)	124.3	220.1	300.2	280.6

larger with decreasing cell volume as the VEC is increased by replacing Y with Zr and subsequently with Nb. As expected, the bulk modulus shows opposite behavior to the cell volume. This means that the shorter M-C bond length gives rise to a larger bulk modulus of the corresponding carbide due to stronger covalent bonding between metal and carbon. Since bulk modulus measures the resistance of a material to a volume change, it is directly correlated to the bond strength between adjacent atoms. The variation of bulk modulus with the valence electron concentration of MC reflects the fact that the mechanical hardness of these compounds is determined by the occupation of the M 4d-C 2p bonding states. The decreasing bulk modulus of RhC is related to the partial occupation of the M 4d-C 2p antibonding states. The effect of VEC on the elastic properties of the studied MC compounds is discussed in terms of chemical bonding between metal and carbon.

Electronic and Bonding Properties. In order to understand the nature of the electronic band structures of MC (M = Y, Zr, Nb, Rh) compounds, we have calculated the DOS for these compounds. The calculated DOS plots are displayed in Figure 1. The overall DOS profiles are quite similar. A non-vanishing DOS at the Fermi level explains the metallic

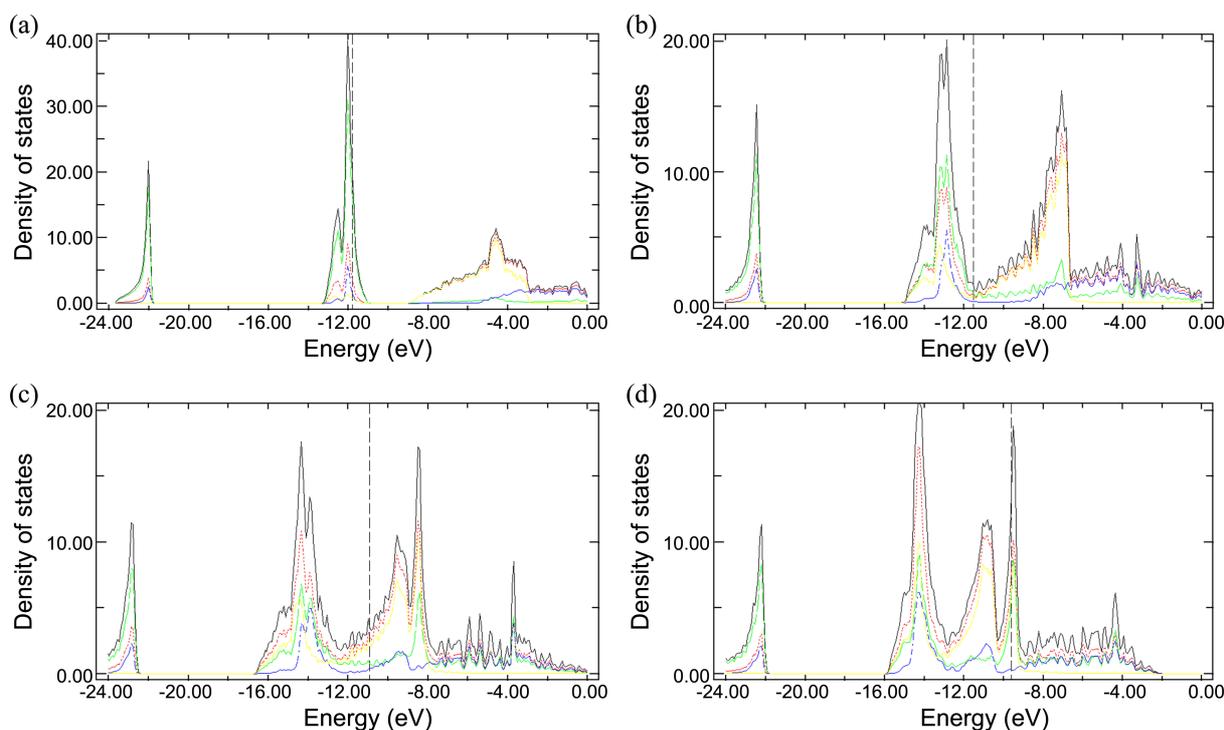


Figure 1. Total DOS (black line) and the contributions of metal (red line), carbon (green line), e_g (blue line), and t_{2g} (yellow line) orbitals to it in (a) YC, (b) ZrC, (c) NbC, and (d) RhC. The vertical dashed line denotes the Fermi level.

character of the metal carbides. They are decomposed into three well separated regions: (i) a deeply bound lowest valence band (LVB); (ii) a filled (or, for YC, partially filled) upper valence band (UVB); (iii) an empty (or, for RhC, partially filled) conduction band (CB).

The LVB, peaked below -22 eV, is dominated by the 2s orbitals of the carbon atoms, with only small contributions of the M 4d orbitals. Since the C 2s level is significantly more tightly bound than the metal 4d band, there is relatively little interaction between them. Therefore, the contribution of this band to the bonding is presumably not so large.

The filled UVB is mainly composed of carbon 2p and transition metal 4d orbitals. These peaks correspond to the M-C bonding states, and their antibonding counterparts except RhC appear above the Fermi level. The M-C bonding is primarily covalent, because the states of M and C atoms are strongly mixed together. In ZrC, the Fermi level falls at a minimum of the DOS in the pseudogap between the UVB and the CB. As one moves along the 4d series from Y to Nb, the number of valence d electrons increases and the position of 4d orbitals shifts toward the lower energy, giving a better energy overlap between the M 4d and C 2p orbitals. The strengthening of the interaction can be simply explained by the decrease of the energy separation between the M 4d and C 2p orbitals. The M 4d-C 2p bonding region also shifts to the lower energy on going from YC to NbC. This shift toward lower energies is caused by more extensive mixing between metal 4d and C 2p orbitals. As a consequence, Nb 4d-C 2p bonding states are located deeper in energy below the Fermi level and much more delocalized as the Nb 4d orbitals lie closer to C 2p in energy than the other metal 4d orbitals. It is

-13 to -11 eV for YC, -15 to -11.5 eV for ZrC, and -16.5 to -12.5 eV for NbC. One can clearly see that this band lies lower and becomes broader on going from YC to NbC. So we can deduce that M-C covalent interactions in these compounds are strongest in NbC and reduced in YC. The substitution of the transition metal Y by Zr and further by Nb leads to the filling of additional valence electrons in the bonding states of M 4d-C 2p bands. This band filling correspondingly causes an increase in the strength of M to C bonding and then the bulk modulus of MC.

The CB is mainly composed of the antibonding states of the M-C covalent interaction, dominated by the metal 4d states, but with substantial contribution from carbon 2p orbitals. Due to the octahedral symmetry around the M site in rocksalt MC, the metal d orbitals split into orbitals of e_g (i.e., x^2-y^2, z^2) and t_{2g} (i.e., xy, yz, xz) sets. This splitting arises through orbital interactions between M 4d and C 2p orbitals, just as in molecular transition metal complexes. The e_g orbitals point toward the nearest C-atom sites, while the t_{2g} orbitals are directed between them. The t_{2g} levels are destabilized by metal-carbon π interactions. Analogously, the e_g orbitals are further destabilized by M-C nearest-neighbor δ interactions. Our calculated DOS (Figure 1), projected onto metal e_g and t_{2g} orbitals, confirms that the e_g orbitals have higher energy than the t_{2g} orbitals. The e_g orbitals can form a p-d σ bond with carbon 2p orbitals. Similarly, t_{2g} orbitals are involved in p-d π interactions with carbon 2p orbitals of the correct symmetry. At the same time, these t_{2g} orbitals may remain M-C σ nonbonding states located only on the metal and form d-d σ bonds between neighboring metal atoms. The projected DOS curves show that the metal

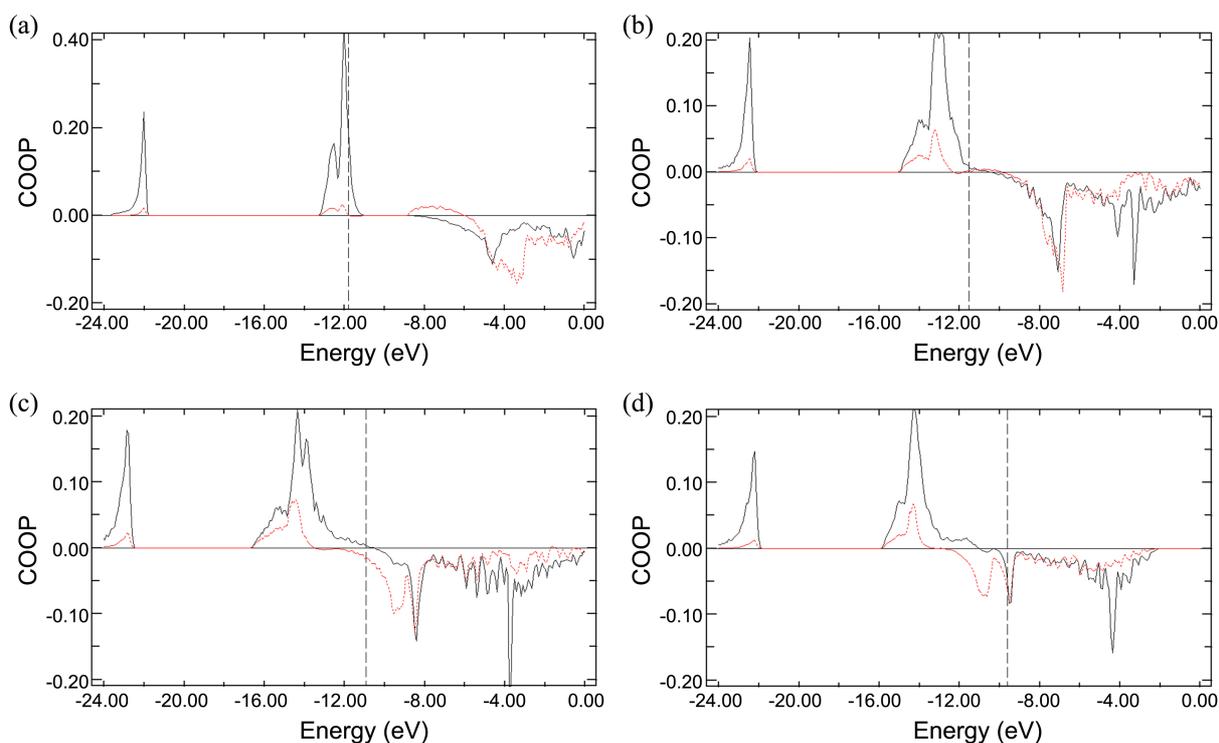


Figure 2. Crystal orbital overlap populations for the metal-C (black line) and metal-metal (red line) bonds in (a) YC, (b) ZrC, (c) NbC, and (d) RhC. The vertical dashed line denotes the Fermi level.

d states are predominant in both the UVB and the CB. This result confirms the mixed covalent M-C and metallic M-M bonding nature. A bonding and an antibonding M-M character are identified in the UVB and the CB, respectively. Hence, the metal atoms play two roles for the bonding in the metal carbides, by their interactions with the C atoms and with other metal atoms.

To more closely examine the bonding character of the rocksalt MC crystal orbitals, we present the COOP curves of Figure 2. These curves indicate the bonding (or antibonding) nature of the crystal orbitals as a function of level energy. Where the curves are positive the orbitals are bonding, where negative they are antibonding. We confirm the bonding character present in the UVB and CB, regarding the M-C and M-M bonds in bulk MC. It can be observed from the DOS and COOP patterns that Zr 4d-C 2p bonding states are completely filled for ZrC with eight valence electrons per formula unit. The Fermi level is located in a pseudogap of the DOS, which separates the bonding from the nonbonding (or antibonding) states. But in the case of NbC, the additional valence electrons cause the Fermi level to rise above this pseudogap and hence nonbonding metal t_{2g} states are partially filled. This may not modify the bonding properties significantly. We emphasize, however, that the filling of broader bonding peaks below the pseudogap in NbC yields an intrinsically stronger Nb-C bond than that of the corresponding peaks in ZrC. Notice that the overall metal-C bond strength is best for the NbC system. In YC, on the other hand, not all the bonding states are filled for the interaction of the C 2p with the Y 4d orbitals. As Y is replaced with Zr and subsequently with Nb, the bonding interactions between metal 4d and carbon 2p orbitals should rise to a maximum, suggesting an increase in the M-C bond strength and hence the bulk modulus. As Nb is replaced with Rh, more valence d electrons are added to the metal atom and they occupy the Rh 4d-C 2p antibonding states. This suggests that the metal-C bonds are somewhat weaker in RhC than in NbC. Therefore, the reduction in Rh-C bond strength and bulk modulus in RhC is expected to result from this band filling effect.

We have shown that bulk modulus in MC compounds can be understood by considering the changes in the electronic structure and M-C bond strength associated with increasing the number of valence electrons of the transition metal. The COOP provides valuable insight to understand the nature of the chemical bonding controlling their properties, which can be assessed further by Mulliken population analysis. The bond overlap population (OP) based on Mulliken population analysis can be used as a measure of the strength of the covalent bonding between atoms. The covalent strength of a specified bond can be determined by the total overlap population obtained by summing up the area under the COOP curve up to the Fermi level. We list in Table 3 the calculated overlap population per single bond and bond distances for M-C and M-M bonds in all the studied compounds. The magnitude of overlap populations is *ca.* 0.31-0.41 for M-C bonds in these compounds. The M-C distances in all

Table 3. Overlap populations (OP) for M-C and M-M bonds in MC (M = Y, Zr, Nb, Rh)

Compound	Bond	Bond length (Å)	OP
YC	Y-C	2.545 (2.388) ^a	0.31
	Y-Y	3.599 (3.232)	0.02
ZrC	Zr-C	2.355 (2.226)	0.40
	Zr-Zr	3.330 (2.908)	0.07
NbC	Nb-C	2.245 (2.116)	0.41
	Nb-Nb	3.175 (2.684)	0.09
RhC	Rh-C	2.180 (2.024)	0.34
	Rh-Rh	3.083 (2.504)	-0.03

^aThe sum of single-bond radii for a given pair of atoms is presented in parentheses.²⁰

compounds are a bit larger than the sum of single-bond radii for metal and carbon atoms.²⁰ Presumably strong orbital interactions of metal with carbon should be expected. The increase in OP values of the M-C bonds from YC to ZrC to NbC indicates that there occurs a gradual strengthening of M-C bonds. However, the Rh-C bond in RhC is weakened compared to the Nb-C bond in NbC, which leads to a significant decrease in its OP value. The elastic properties in MC (M = Y, Zr, Nb, Rh) compounds are strongly related to the covalent strength of M-C bonds. More filling of M 4d-C 2p bonding states in YC, ZrC, and NbC increases the M-C bond strength, which nicely explains the larger bulk modulus. In the case of RhC, the partially filling of Rh 4d-C 2p antibonding states reduces the strength of the Rh-C bonding and causes the decrease of the bulk modulus.

In the end, the number of valence d electrons of the metal atom, the mixing between C 2p and metal 4d states, and the filling of the bonding and antibonding states arising from it are responsible for the elastic properties of these compounds. The metal-metal distance in these metal carbides is much longer than the nearest-neighbor distance in pure metals. This probably indicates weak bonding interactions between metal atoms in contrast to the strong M-C interaction. As seen in Figure 2, the small bonding peak for M-M bonds results from the long bond distance between them. Therefore, the integrated COOP value is not very large for the M-M bonds (see Table 3). They do not contribute much to the overall bonding of the solids. The minus sign of the overlap population for the Rh-Rh bonds indicates that the interaction between metal atoms is slightly antibonding, which gives a negative contribution to the stability of RhC in the rocksalt structure. This instability can be explained as arising from a fair amount of filling of Rh-Rh antibonding states, as shown in Figure 2(d). In addition, no significant C-C bonds are expected to be present in all the studied carbides because the C-C distances are more than twice longer than the covalent C-C distance (1.54 Å).

Conclusion

We have investigated the correlation between valence electron concentration and elastic properties of MC (M = Y,

Zr, Nb, and Rh) compounds in the rocksalt structure based on EHTB band electronic structure calculations. The results indicate a metallic behavior for these compounds. The bulk modulus is directly related to the number of valence electrons of M and the filling of the p-d bonding states formed by the mixing between C 2p and M 4d orbitals. With the increase in the number of d electrons from YC to NbC, more filling of the bonding states provides the larger overlap population of M-C bonds and thereby the higher bulk modulus. The bulk modulus of RhC with an excessive VEC decreases due to the partial occupation of the p-d antibonding states. These observations are compatible with the mechanical behavior of all the studied compounds.

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