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## Electronic structure of $M_2AlC(0001)$ surfaces ( $M = Ti, V, Cr$ )

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### Abstract

We have studied the correlation between the valence electron configuration and the electronic structure of  $M_2AlC(0001)$  surfaces ( $M = Ti, V, Cr$ ) using *ab initio* calculations. Based on our surface energy data, we find that the Al termination is the most stable configuration. As the M valence electron population is increased, the surface energy increases. This can be understood by analysing the valence electron concentration induced changes of the electronic structure. Antibonding states are present as Ti is substituted by Cr in  $M_2AlC(0001)$ . These results are of relevance for vapour phase condensation as well as oxidation.

In terms of electronic structure, nanolaminates can be described as interleaved layers of high and low electron density [1]. MAX phases can thus be referred to as nanolaminates since they consist of periodically alternating MX ( $M =$  early transition metal,  $X = C$  or  $N$ ) and A layers ( $A =$  mostly IIIA and IVA elements) [2, 3]. In general, these ternary phases are good thermal and electrical conductors, resistant to oxidation, as well as exhibiting extensive plasticity [2, 3]. After the publication of a seminal review paper on MAX phases in 2000 [2], more than 150 articles discussing the properties of MAX phases have been published. However, surface studies are still lacking in the literature. Generally, such data are important for understanding the thin film synthesis [4, 5], oxidation kinetics [6, 7] and plasticity [8–10] of MAX phases and other nanolaminated solids.

Recently, Sun and Ahuja have studied (0001) surfaces of  $Cr_2AlC$  [11] and found that the Al termination is the most stable due to smallest surface energy as compared to Cr and C terminations. In terms of electronic structure, the surface density of states (DOS) was compared with the bulk counterpart and no significant changes were observed, which implies that the changes in bonding are minute. However, a systematic study of the effect of the valence electron

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**Table 1.** Surface energy of  $M_2AlC(0001)$ , where  $M = Ti, V, Cr$ . M, Al and C stand for transition metal, aluminium and carbon terminations, respectively.

	Surface energy ( $J m^{-2}$ )		
	M	Al	C
$Ti_2AlC(0001)$	5.264	1.974	5.262
$V_2AlC(0001)$	5.403	2.312	5.402
$Cr_2AlC(0001)$	5.357	2.409	5.358

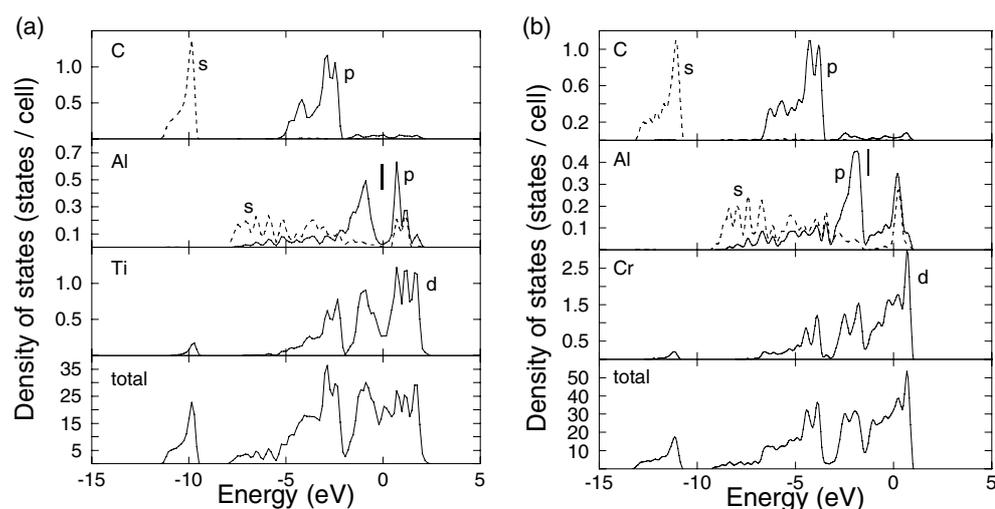
concentration of the transition metal on the MAX-phase surface energies is not available in the literature.

In this work, we systematically study  $M_2AlC(0001)$  surfaces ( $M = Ti, V, Cr$ ) using *ab initio* calculations. These phases crystallize in the  $P6_3/mmc$  space group with the  $Cr_2AlC$  prototype [2, 3]. It is our ambition to correlate the valence electron configuration of M with the electronic structure of these surfaces. Based on the surface energy data, Al termination yields the most stable configuration. As the valence electron population is increased by replacing Ti with V and further with Cr, the surface energy increases. This can be understood by analysing the electronic structure associated with the formation of the surface.

*Ab initio* calculations were used for all calculations in this work, which are implemented in the Vienna *ab initio* simulation package (VASP). Ultra-soft pseudopotentials and the generalized gradient approximation were applied [12, 13], with the so-called Blöchl corrections for the total energy [14]. The integration in the Brillouin zone is done on special  $k$ -points determined according to the Monkhorst–Pack method [15]. First, these ternary carbides with eight atoms in a unit cell were relaxed with respect to the atomic positions, lattice parameter  $a$ , i.e. Wigner–Seitz primitive cell volume, and their hexagonal  $c/a$  ratios. Then, (0001) surfaces with all possible terminations were constructed.  $2 \times 2 \times 1$  supercells containing 32 atoms (8 atomic layers) were studied on a mesh of  $7 \times 7 \times 5$  irreducible  $k$ -points. The  $k$ -point conversion was tested on  $3 \times 3 \times 3$ ,  $5 \times 5 \times 5$ ,  $7 \times 7 \times 7$  and  $7 \times 7 \times 5$  meshes and the total energy conversion of 0.004 meV/atom was achieved (cutoff energy 400 eV). The total and partial DOSs as well as the surface energy [11] were calculated.

We start the analysis of the  $M_2AlC(0001)$  surfaces by discussing the stability thereof. In table 1, all surface energies are given. The data on  $Cr_2AlC(0001)$  are taken from [11]. M and C terminations possess by a factor of 2.2–2.7 larger surface energy than that of the corresponding Al termination. Hence, Al termination yields the most stable configuration due to the smallest surface energy. As the valence electron population is increased by substitution of Ti with V and further with Cr, the surface energy increases from 1.97 to 2.41  $J m^{-2}$ , by 22.3%. This may be understood by analysing the electronic structure, as discussed below. Furthermore, based on previously published data it is expected that the layered compounds do not exhibit significant surface reconstructions [16, 17]. Indeed, all surfaces examined do not reconstruct and we observe surface relaxations only. The V and Cr terminations exhibit surface relaxations from 6.5% to 23.6%, while the Al terminations relax from 1.7% to 3.1%. These results are relevant for the oxidation behaviour: as the surface is terminated by Al, the onset of oxidation is expected to be governed by the interaction of these elements. In the case of Al containing MAX phases,  $Al_2O_3$  may form, hindering further oxidation by surface passivation. This notion is consistent with previously reported experimental results of the stability of the MAX phases discussed here [7, 18–20].

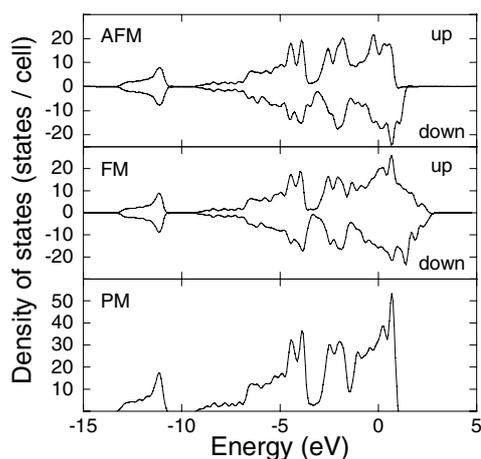
In figure 1, the total and partial DOS data of the Al-terminated  $M_2AlC$  phases ( $M = Ti$  and Cr) are shown. General features of the total DOS data for the bulk  $M_2AlC$  have been



**Figure 1.** Total and partial density of states for (a)  $Ti_2AlC$  and (b)  $Cr_2AlC(0001)$  surfaces terminated with Al. The Fermi energy is set to 0 eV and the vertical tick indicates the position of the pseudogap.

analysed previously [21–25]. The deepest core states correspond to C 2s orbitals; M 3d–C 2p hybridization dominates from approximately  $-7$  to  $-4$  or  $-2$  eV for  $M = Cr$  or  $Ti$ , respectively. M 3d–Al 3p hybridization is present just below the Fermi level and the Fermi level is mostly occupied by M 3d electrons [21–25]. As the valence electron population is increased by substitution of  $Ti$  with  $V$  and further with  $Cr$ , the most dominant change in the total DOS data is the shift of the pseudogap in the M 3d–Al 3p hybridization from approximately  $-1.7$  eV for  $M = Ti$  to approximately  $-3.5$  eV for  $M = Cr$  [25]. This pseudogap may split bonding and antibonding states and implies that the M–Al bond strength is a function of the valence electron population, which is consistent with previous work [25–27]. There is no significant difference between the surface and the bulk total DOS [11], indicating resemblance in the chemical bonding. This is also consistent with the absence of significant surface reconstructions, as reported in [11]. Furthermore, main contributions to the surface energy may be related to band filling effects, which are discussed in the literature [21, 23, 24]. For  $Ti_2AlC$  (figure 1(a)), it is apparent that Al 3p states are shifted towards higher energies as the Al-terminated (0001) surface is formed. This suggests that antibonding states in the Ti 3d–Al 3p hybridization, originally occupied at the Fermi level, are above the Fermi level of the Al-terminated (0001) surface (figure 1(a)). This is a particularly stable configuration since the bonding and antibonding states are symmetrical with respect to the Fermi level [28]. For  $Cr_2AlC$  (figure 1(b)), Al 3p states also shift towards higher energies, but the antibonding states in the Cr 3d–Al 3p hybridization are still occupied when the Al-terminated (0001) surface is formed. Hence,  $Cr_2AlC(0001)$  is expected to possess a larger surface energy than  $Ti_2AlC(0001)$ , which is consistent with the data in table 1. Furthermore, these data are consistent with the bond energy data published previously [21]. Besides the relevance for oxidation kinetics, the results presented may also be important for modelling structure evolution during thin film growth from the vapour phase.

Even though the differences induced by spin polarization for the total energy of bulk  $Cr_2AlC$  [5] and  $V_2AlC$  [29] were previously determined to be minute, we consider spin polarization for Al-terminated  $Cr_2AlC(0001)$ . The surface energy and local magnetic moment



**Figure 2.** Total DOS data for paramagnetic (PM), ferromagnetic (FM) and antiferromagnetic (AFM) configurations of Al-terminated  $\text{Cr}_2\text{AlC}$  (0001). The Fermi energy is set to 0 eV.

**Table 2.** Surface energy ( $E_s$ ) and local magnetic moment ( $m$ ) of Al-terminated  $\text{Cr}_2\text{AlC}$ (0001) for paramagnetic (PM), ferromagnetic (FM) and antiferromagnetic (AFM) configurations. The surface energy is given with respect to the PM configuration, while  $m$  at the Cr site is provided for all Cr layers, where 1 designates the layer closest to the surface.

	$E_s$ ( $\text{J m}^{-2}$ )	$m_{\text{Cr1}}$ ( $\mu_B$ )	$m_{\text{Cr2}}$ ( $\mu_B$ )	$m_{\text{Cr3}}$ ( $\mu_B$ )	$m_{\text{Cr4}}$ ( $\mu_B$ )
PM	0.000	—	—	—	—
FM	-0.020	1.08	0.33	0.14	-0.07
AFM	-0.063	2.30	-0.13	-0.14	0.02

for paramagnetic (PM), ferromagnetic (FM) and antiferromagnetic (AFM) configurations of Al-terminated  $\text{Cr}_2\text{AlC}$ (0001) are given in table 2. The AFM configuration is by  $0.063 \text{ J m}^{-2}$  more stable than the PM configuration. In the bulk  $\text{Cr}_2\text{AlC}$  [5], it was not possible to establish whether the PM or AFM configuration was more stable due to the minute energy difference. On the other hand, formation of the (0001) surface stabilizes the AFM configuration with the local magnetic moment of  $2.30 \mu_B$  for the Cr layer closest to the Al surface. In the bulk  $\text{Cr}_2\text{AlC}$  [5], bulk bcc Cr [30] and isolated Cr atoms on Au(111) surface [31], the local magnetic moment at the Cr site is  $0.64$ ,  $0.45$  and  $3.93 \mu_B$ , respectively, which implies that surface effects and the stacking sequence of Cr atoms are relevant for the spin polarization thereof. Therefore, magnetism may play a role for  $\text{Cr}_2\text{AlC}$ (0001) at 0 K. Due to the small differences in the surface energy between the different magnetic configurations, we expect no magnetism at elevated temperatures. We explore the effect of spin polarization on the electronic structure. In figure 2, total DOS data are given for the PM, FM and AFM configurations of Al-terminated  $\text{Cr}_2\text{AlC}$ (0001). The total DOS data for the FM and the AFM configuration are rather similar to the total DOS data for the PM configuration; hence spin polarization does not significantly affect the electronic structure.

In conclusion, we have studied the correlation between the valence electron configuration and the electronic structure of  $\text{M}_2\text{AlC}$ (0001) surfaces ( $\text{M} = \text{Ti}, \text{V}, \text{Cr}$ ) using *ab initio* calculations. For all phases studied in this work, the Al termination is the most stable due to the smallest surface energy. As the valence electron population increases by replacing Ti with V and further with Cr, the surface energy increases by 22.3%. This can be understood by

analysing the electronic structure changes associated with the formation of the surface.  $M 3d$ – $Al 3p$  hybridization is present in the vicinity of the Fermi level for all  $M_2AlC$  phases, giving rise to splitting of bonding and antibonding states. Antibonding states are present as  $Ti$  is substituted by  $Cr$  in  $M_2AlC(0001)$ . Hence, it is expected that  $Cr_2AlC(0001)$  possess a larger surface energy than  $Ti_2AlC(0001)$ . These results may have importance for understanding the thin film synthesis thereof and initial stages of oxidation.

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