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2005 J. Phys.: Condens. Matter 17 7169

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Electronic origin of shearing in M_2AC ($M = Ti, V, Cr, A = Al, Ga$)

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Received 25 July 2005

Published 1 November 2005

Online at stacks.iop.org/JPhysCM/17/7169

Abstract

We have studied shearing in M_2AC (space group $P6_3/mmc$, prototype Cr_2AlC), where M is Ti, V and Cr , and A is Al and Ga , using *ab initio* calculations. These compounds can be described as interleaved layers of MC and A . As Ti in Ti_2AlC is substituted by V , c_{44} increases by 24.3%. Increasing the transition metal valence electron concentration further, through a substitution of V by Cr , results in 2.2% decrease of c_{44} . The electronic origin of this c_{44} versus valence electron concentration dependence may be understood by analysing the decomposed band structure: in the vicinity of the Fermi level, we find two types of dd bonding. One contributes to shearing ($t_{2g} + e_g$ symmetry or MC – MC coupling) and the other does not (e_g symmetry). We provide evidence that filling of the transition metal dd bonding states with the $t_{2g} + e_g$ symmetry may be responsible for the behaviour of c_{44} . The results presented enable tailoring of the shear properties of M_2AC phases.

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

1. Introduction

Transition-metal carbides and nitrides are commonly applied as hard coatings and refractory compounds. Using *ab initio* calculations, their hardness is usually discussed in relation to the elastic constant c_{44} , since it provides shearing-related information. It has been reported that the transition-metal carbonitrides (space group $Fm\bar{3}m$, prototype $NaCl$) exhibit the maximum c_{44} for the valence-electron concentration (VEC) in the range of 4.15–4.25 per atom [1]. Band structure analysis has revealed that the pd bonding states are particularly resistant to shearing. Filling of these states is completed for the VEC in the range of 4.15–4.25 per atom, which is consistent with the VEC of approximately 4.2 per atom where the experimentally determined

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hardness values for the transition metal carbonitrides reach the maximum [2–4]. Shearing in another ternary transition metal carbide has recently been suggested: M_2AlC phases ($M = Ti, V, Nb$ and Cr) have been reported to exhibit the maximum c_{44} for the VEC in the range of 4.2–4.3 per atom [5]. Based on the analysis of the charge-density distribution with no shear strain applied, it has been suggested that, in analogy to the transition metal carbonitrides discussed earlier, the $M\ d$ – $Al\ p$ bonding states are resistant to shearing. Furthermore, it was proposed that the $M\ d$ – $M\ d$ bonding states are not resistant to shearing [5]. It is our ambition to contribute towards understanding the electronic origin of shearing in these ternary compounds. We have therefore carried out a detailed analysis of the bonding states in unstrained and in strained M_2AC ($M = Ti, V, Cr$ and $A = Al, Ga$).

These ternary carbides belong to a family of layered solids with a stoichiometry $M_{n+1}AC_n$, where M is an early transition metal, A is an A-group element and $n = 1$ – 3 . They are referred to as nanolaminates because MX layers are interleaved with A layers, which in turn gives rise to an unusual combination of properties. We have shown that M_2AC can be classified into two groups: one where the bulk modulus of the binary MC is conserved and another group where the bulk modulus is decreased [6]. This classification can be understood in terms of coupling between MX and A nanolaminates. Intensive studies suggest that M_2AC phases may be technologically important compounds due to their unique combination of metallic and ceramic properties [7–11]. However, as pointed out earlier, the electronic origin of shearing in M_2AC is not understood.

In this work, we have systematically investigated c_{44} as a function of VEC for M_2AC ($M = Ti, V, Cr, A = Al, Ga$) and changes in the electronic structure upon shearing. It is our ambition to shed light on the electronic origin of shearing in M_2AX phases. We present evidence that filling of the transition metal dd bonding states with the $t_{2g} + e_g$ symmetry increases the shear resistance. These bonding states correspond to the MC – MC coupling in these layered phases. Hence, the electronic origin of the shear properties is different as compared to the previously investigated transition metal carbonitrides [1]. Our findings are of importance since the shear properties of M_2AC can be tailored based on the density of transition metal dd bonding states with the $t_{2g} + e_g$ symmetry.

2. Calculation methods

The calculation method used is based on density functional theory using the VASP code [12, 13], in conjunction with the projector-augmented wavefunctions wherein the generalized-gradient approximation [14] is employed. The following parameters were applied in our calculations: relaxation convergence for ions and electrons was 1×10^{-4} and 1×10^{-5} eV, respectively, conjugate gradient optimization of wavefunctions, reciprocal-space integration with the Monkhorst–Pack scheme [15], energy cut-off of 500 eV, k -point grid of $7 \times 7 \times 7$ and the tetrahedron method with Blöchl corrections for the total energy [16]. To calculate c_{44} , shear strains up to 2% were used on the relaxed hexagonal lattice (space group $P6_3/mmc$, prototype Cr_2AlC), resulting in the triclinic symmetry. Thus, c_{44} is derived from the functional dependence of the total energy with shear strain [17]. Test calculations comparing c_{44} values obtained from relaxed and unrelaxed structures after applying the shear strain suggest a <10% difference in c_{44} . Therefore, we have decided not to relax the deformed crystal. To understand the electronic origin of shearing, the band structure and decomposed charge density distribution were calculated. In order to make the difference between equilibrium and strained structures clearer, a shear strain of 10% was applied when calculating the band structure of M_2AC under shear.

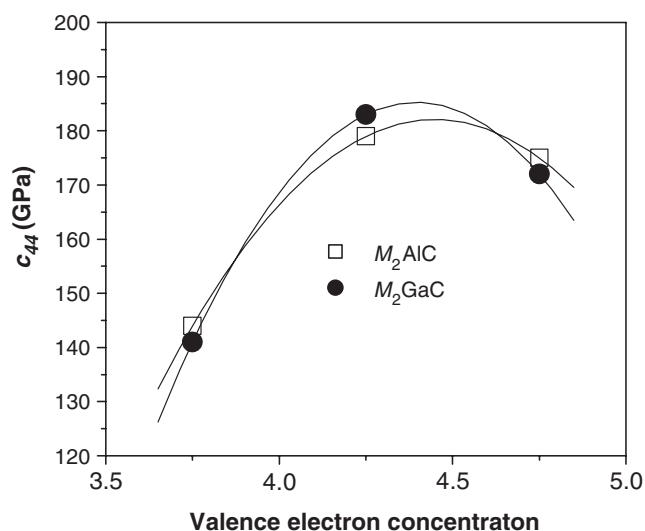


Figure 1. Calculated elastic constants c_{44} of M_2AC ($M = \text{Ti, V, Cr, A} = \text{Al, Ga}$) as a function of valence electron concentration per atom. Solid lines represent a third-order polynomial fit.

3. Results and discussion

3.1. Analysis of elastic constant c_{44}

Figure 1 shows the calculated elastic constant c_{44} of M_2AC ($M = \text{Ti, V, Cr, A} = \text{Al, Ga}$) as a function of VEC. As the VEC ($A = \text{Al}$) is increased from 3.75 to 4.25 per atom, c_{44} increases from 144 to 179 GPa, by 24.3%, and then decreases to 175 GPa, by 2.2%, for the VEC of 4.75 per atom. It is evident that c_{44} exhibits the maximum value for the VEC value of 4.35 per atom utilizing a polynomial fit as in the literature [1, 5]. This is consistent with the literature on $M_2\text{AlC}$ ($M = \text{Ti, V, Nb, Cr}$) [5] and transition metal carbonitrides with a rock-salt structure [1]. Furthermore, it is worth noting that the A elements do not significantly affect c_{44} for the M_2AC phases studied. This may be understood based on the partial density of states analysis of elastic behaviour of M_2AC ($M = \text{Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W}$ and $A = \text{Al, Ga, Ge, Sn}$) [6] under isostatic compression. As Al in Cr_2AlC is substituted with Ge, there are no significant changes in the bonding. In order to understand the behaviour of c_{44} , we study shearing induced changes in electronic structure of $M_2\text{AlC}$ ($M = \text{Ti, V, Cr}$).

3.2. Band structure analysis

In figure 2, the band structure of Ti_2AlC , V_2AlC and Cr_2AlC along the high-symmetry lines of the first Brillouin zone is given. No shear strain was applied. In Ti_2AlC (figure 2(a)) 15 bands can be filled completely and for the Γ -point the Fermi level is located in a valence band maximum (13th band). Based on the partial density of states analysis [5, 6], the role of these bands for the chemical bonding can be understood. The M d-C p hybridized states are totally filled and located far from the Fermi level, while the hybridized M d-A p states are very close to the Fermi level, which is dominated by the M d states. Therefore, the 13th band and others located higher in energy may contribute to pd and dd bonding. As Ti is replaced with V (figure 2(b)), 17 bands can be filled completely and the Fermi level shifts by 2.4 eV. At the Γ -point the Fermi level is located at a local minimum. This shift suggests that more valence

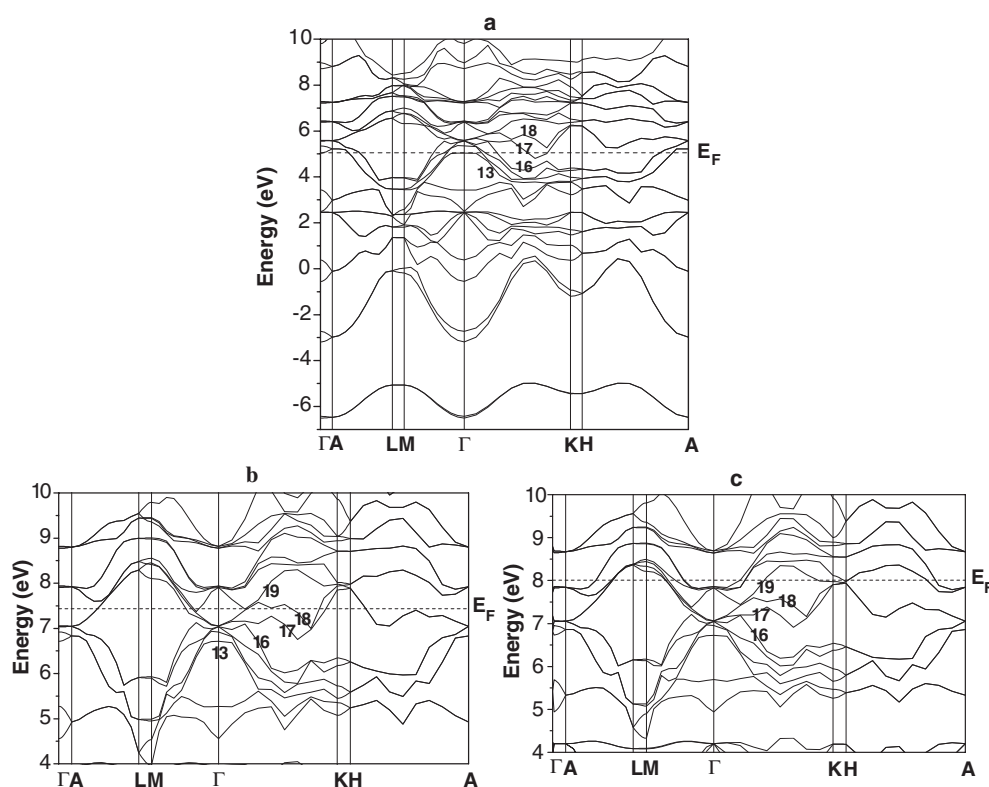


Figure 2. Band structure with no shear strain applied for (a) Ti_2AlC , (b) V_2AlC and (c) Cr_2AlC . Vertical lines represent high-symmetry points of the hexagonal Brillouin zone. The horizontal dashed line designates the Fermi level (E_F) and the bands in its vicinity are numbered.

electrons fill the bonding states, resulting in an increase in strength [18, 19]. Furthermore, this also implies that there are changes in the chemical bonding since the hybridized M d–A p orbitals and the M d states become occupied [6]. As V is replaced with Cr (figure 2(c)), 19 bands can be filled completely and for the Γ -point the Fermi level shifts by 0.6 eV. The Fermi level is still located at a local minimum. This smaller shift of the Fermi level may suggest that the hybridized M d–A p states are partly filled in V_2AlC and totally filled in Cr_2AlC , which may account for the smaller strength difference between Cr_2AlC and V_2AlC as compared to V_2AlC and Ti_2AlC [18, 19].

After analysing the unstrained band structure, the discussion is continued with the strained band structure, as provided in figure 3. Some general remarks can be made with respect to the effect of strain. Firstly, originally degenerate bands are split under strain because of symmetry breaking. Secondly, there are significant changes along the M– Γ –K line near the Fermi level. The 13th and 14th bands move to a lower energy level, while the 15th band is not affected. This suggests that these bands are resistant to shearing. The 16th, 17th and 18th bands, originally degenerate at the Γ -point, split upon shearing and move to a higher energy level: close to the Fermi level in the case of V_2AlC and Cr_2AlC , but above the Fermi level for Ti_2AlC . Hence, it is likely that the 16th, 17th and 18th bands are very sensitive to shearing and may play a crucial role for the understanding thereof.

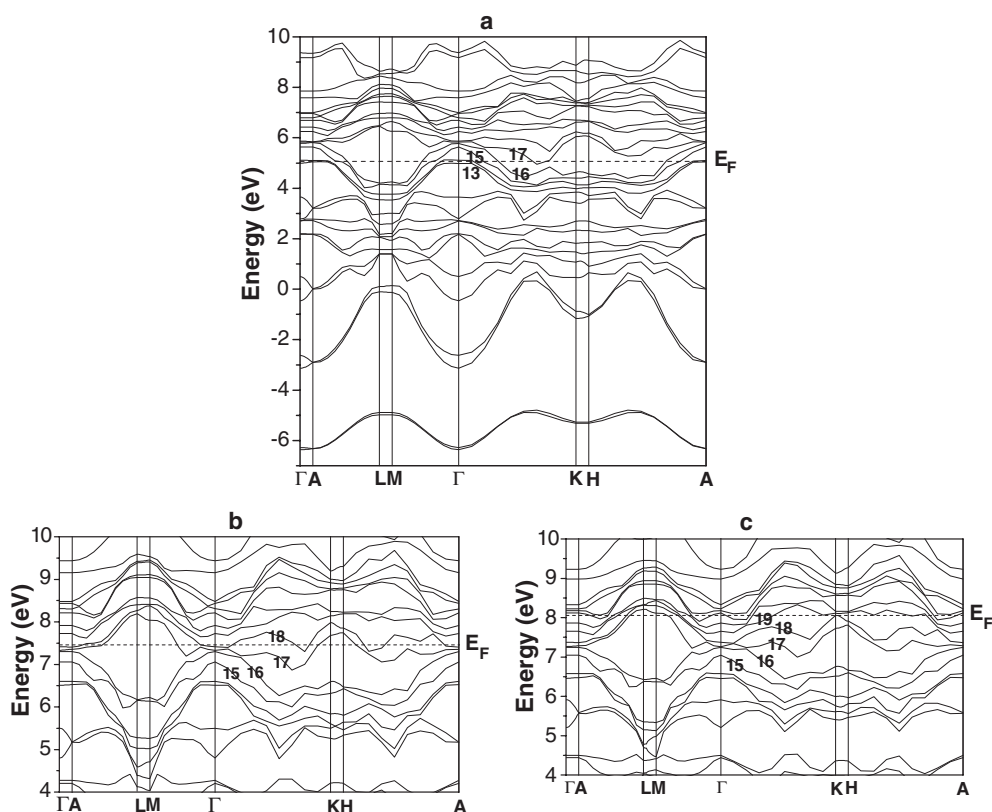


Figure 3. Band structure with the shear strain of 0.1 for (a) Ti_2AlC , (b) V_2AlC and (c) Cr_2AlC . Vertical lines are high-symmetry lines equivalent to that of the hexagonal structure. The horizontal dashed line indicates the Fermi level (E_F) and the bands in its vicinity are numbered.

3.3. Decomposed charge-density distribution analysis

The decomposed charge-density distribution of unstrained Ti_2AlC , V_2AlC and Cr_2AlC is given in figures 4, 5 and 6, respectively. For Ti_2AlC , it can be observed that electrons filling the 14th band contribute to the Ti d–Al p bonding states (figure 4(a)), while those filling the 15th (figure 4(b)) and 16th (figure 4(c)) bands give rise to strong dd bonding with the $t_{2g} + e_g$ symmetry, which is responsible for the MC–MC coupling. The 17th band (figure 4(d)) contributes to the dd bonding with the e_g symmetry. This implies that the Ti d–Al p states are completely filled up to the 16th band. The character of the decomposed charge-density distributions for V_2AlC and Cr_2AlC is similar to that of Ti_2AlC . Again, electrons filling the 16th band (figures 5(a) and 6(a)) contribute to the strong dd and weak pd bonding. Further filling the 17th (figures 5(b) and 6(b)) and 18th (figures 5(c) and 6(c)) bands contributes to the weak dd bonding with the e_g symmetry.

The decomposed charge-density distributions discussed above are affected by shearing. In figure 7, the decomposed charge-density distributions is shown in the $(1\bar{1}20)$ plane for Ti_2AlC with the applied shear strain of 0.1. It can be deduced that the 14th–16th bands (figures 7(a)–(c)) are resistant to shearing since the bonds are not broken, while the dd bonding with the e_g symmetry (17th band) is not (figure 7(d)). Figure 8 shows the corresponding decomposed charge-density distributions for V_2AlC and Cr_2AlC upon shearing. Similarly, the 16th band

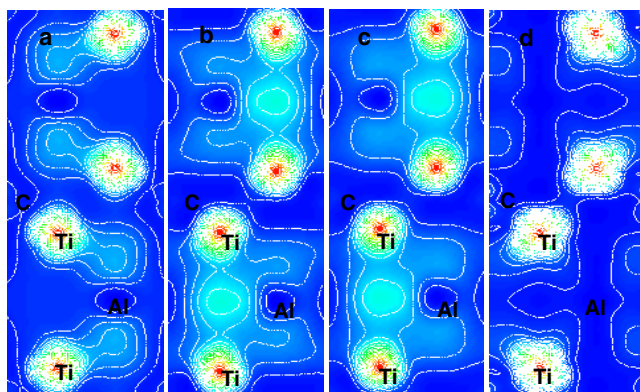


Figure 4. Decomposed charge-density distribution of Ti_2AlC near the high-symmetry k -points of the first Brillouin zone with no shear strain applied. The charge-density plot is given in the $(11\bar{2}0)$ plane for the (a) 14th, (b) 15th, (c) 16th and (d) 17th bands. The charge-density values vary from 0.0 (blue/grey) to 0.35 electrons \AA^{-3} (red/black).

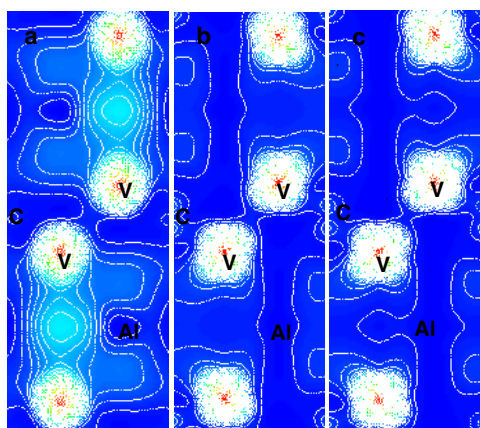


Figure 5. Decomposed charge-density distribution of V_2AlC near the high-symmetry k -points of the first Brillouin zone with no shear strain applied. The charge-density plot is shown in the $(11\bar{2}0)$ plane for (a) 16th, (b) 17th and (c) 18th bands. The charge density scale is the same as in figure 4.

(figures 8(a) and (c)) is resistant to shearing, while the 17th band (figures 8(b) and (d)) is not. Therefore, as Ti is substituted by V and further by Cr, more electrons start to occupy additional bands at the Γ -point, which results in an enhancement of c_{44} . When the VEC reaches 4.35 per atom (based on the polynomial fit), the 16th band at the Γ -point should be completely filled, which results in the maximum value of c_{44} . The decrease of c_{44} upon further increase of the VEC is attributed to the continuous filling of the 17th and 18th bands at the Γ -point. These bands are not resistant to shearing, as discussed above. Therefore, the occurrence of the c_{44} maximum for the VEC of 4.35 per atom is most likely due to the filling of the shear-resistant dd bonding states with the $t_{2g} + e_g$ symmetry near the Fermi level. Wang and co-workers [5] have suggested, based on the band structure analysis with no shear strain applied, that the dd bonding is not resistant to shearing. Here, we identify the MC–MC coupling which governs shearing. Hence, there are two types of dd bonding: one contributes to shearing ($t_{2g} + e_g$ symmetry or MC–MC coupling) and the other does not (e_g symmetry). Consequently, shearing in transition metal carbonitrides is governed by shear resistant pd bonding states [1], while for the phases

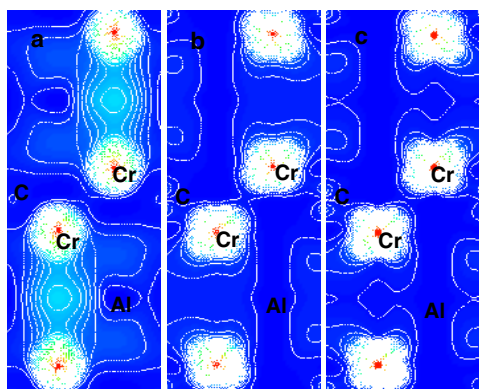


Figure 6. Decomposed charge-density distribution of Cr_2AlC near the high-symmetry k -points of the first Brillouin zone with no shear strain applied. The charge-density plot is given in the $(11\bar{2}0)$ plane for the (a) 16th, (b) 17th and (c) 18th bands. The charge-density scale is the same as in figure 4.

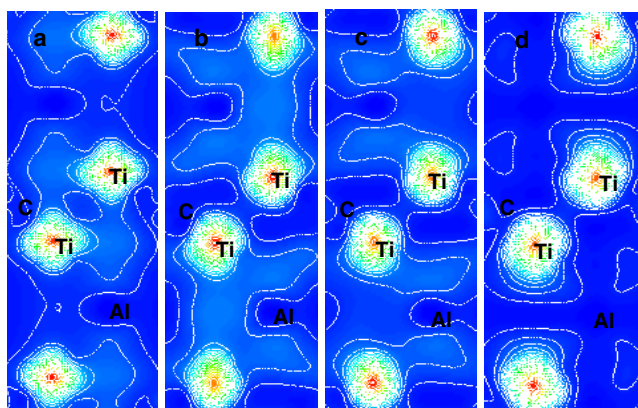


Figure 7. Decomposed charge-density distribution of Ti_2AlC near the high-symmetry k -points of the first Brillouin zone with the shear strain of 0.1. The charge-density plot is in the $(11\bar{2}0)$ plane for the (a) 14th, (b) 15th, (c) 16th and (d) 17th bands. The charge-density values vary from 0.0 (blue/grey) to 0.4 electrons \AA^{-3} (red/black).

investigated here the resistance to shear is governed by dd bonding states. Hence, we have identified the electronic origin of shearing in M_2AC . Based on this mechanism, c_{44} can be tailored: we predict the c_{44} maximum for $(V_{2-x}Cr_x)AlC$ at $x = 0.4$. The formation of $(V_{2-x}Cr_x)AlC$ has been reported experimentally [20] and analysed theoretically [21, 22].

4. Conclusions

We have analysed changes in the electronic structure upon shearing for M_2AC ($M = Ti, V, Cr, A = Al, Ga$) by means of *ab initio* calculations. As Ti in Ti_2AlC is substituted by V , c_{44} increases by 24.3% and then it decreases by 2.2% as V is further substituted by Cr . This may be understood based on the band structure and decomposed charge-density distribution. We showed that the bands near the Fermi level, associated with the $M d$ - $M d$ bonding states, are very sensitive to shearing. Electrons filling these states in the 16th band with the $t_{2g} + e_g$ symmetry may enhance the resistance to shearing and filling of this band may result in a

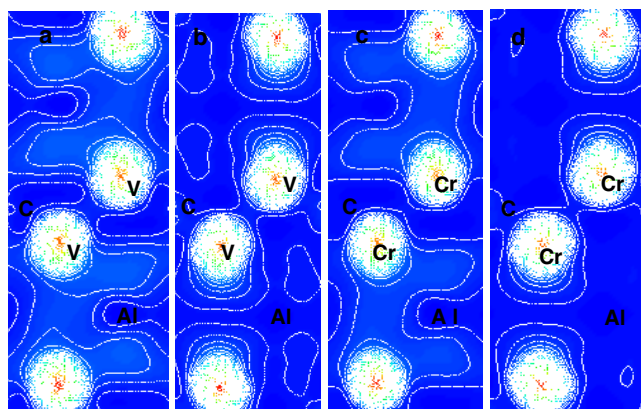


Figure 8. Decomposed charge-density distribution near the high-symmetry k -points of the first Brillouin zone with the shear strain of 0.1. The charge-density plot is in the (1120) plane for the (a) 16th and (b) 17th bands for V_2AlC and the (c) 16th and (d) 17th bands for Cr_2AlC . The charge-density scale is the same as in figure 7.

maximum value of c_{44} . These bonding states correspond to the MC–MC coupling in the layered phases studied. Based on these results the shear properties of M_2AC can be tailored and understood.

Acknowledgments

We acknowledge the financial support granted by the Deutsche Forschungsgemeinschaft (DFG) within the project (Schn 735/8-1) ‘Mechanical properties of MAX phase thin films’. The Swedish Research Council (VR), DAAD and STINT are also gratefully acknowledged.

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