Bonding and classification of nanolayered ternary carbides

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We have investigated the elastic properties of nanolayered M_2AC, with M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W and A=Al, Ga, Ge, Sn, by *ab initio* calculations. We suggest 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. This classification can be understood in terms of coupling between MC and A layers, which is defined by the valence electron population. These results may have implications for the understanding of properties and the performance of this class of solids.

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Transition-metal carbides are suitable for many technological applications due to their high hardness, high melting point, and excellent electrical conductivity. However, the intrinsic brittleness of these carbides hinders their broader applications as structural materials. Owing to a combination of both metallic and ceramic properties, nanolayered ternary metal carbides of $M_{n+1}AC_n$ type (space group $P6_3/mmc$) represent an exception, where $n=1-2$, M is an early transition metal, and A is mostly a IIIA or a IVA group element.[1] For example, Ti_3SiC_2, the most studied $M_{n+1}AC_n$ phase, exhibits an elastic modulus of more than 330 GPa,[1] fully reversible plasticity,[2] and negligible thermopower.[3] Also, M_2AC phases have been investigated both experimentally[1,4–16] and theoretically.[17–22] It is reported that these ternary carbides exhibit improved ductility,[1,15] oxidation resistance,[1,7,9,10] and electrical conductivity.[1,11] They also demonstrate good damage tolerance and thermal shock resistance.[1] However, a systematic correlation between the electronic structure and properties of $M_{n+1}AC_n$ has not been explored in the literature. Here, we discuss the correlation between the chemical bonding and the elastic properties of M_2AC by *ab initio* calculations.

The VASP code[23,24] is used for the present calculations, wherein the generalized-gradient projector-augmented wave potentials are employed.[25] The following parameters were applied: 1×10^{-4} eV relaxation convergence for ions, 1×10^{-5} eV electronic relaxation convergence, conjugate gradient optimization of the wave functions, reciprocal-space integration with a Monkhorst-Pack scheme,[26] energy cutoff of 500 eV, k-points grid of $9 \times 9 \times 9$, and the tetrahedron method with Blöchl corrections[27] for the energy. Spin-polarized configurations were not considered since no significant changes in structures and elastic properties were previously identified for Cr_2AlC (Ref. 28). The equilibrium volume and the bulk modulus were calculated by a least-square fit of the volume-energy curves using the third-order Birch-Murnaghan's equations of states.[29] These volume-energy curves stem from the relaxation of both the lattice parameter a and the hexagonal c/a ratio. The partial density of states and charge-density distributions are obtained using the relaxed structures at the equilibrium volumes. The input lattice parameters of the M_2AC studied are taken from Ref. 1

and those of MC in the NaCl structure as well as TiAl alloy, which are used for the comparison purposes, can be found in Refs. 30–32. In addition, we have also evaluated the hypothetical Mo_2AlC and W_2AC phases, which are not available in literature.

In Fig. 1, we show the calculated bulk moduli of M_2AC versus the bulk moduli of the corresponding MC. It is interesting to note that the bulk moduli of M_2AC are very close to those for MC, except for M_2AC phases containing group IVB transition metals, which show larger deviations. Hence, M_2AC can be classified into two groups according to the transition metal M. One group comprises only group IVB transition metals, where the bulk modulus is reduced compared to the corresponding MC. The other group includes transition metals of groups VB and VIB, where the bulk modulus of the corresponding MC is essentially conserved. Furthermore, it can be seen that for both groups the choice of the A element studied here seems to have no significant effect on the functional dependence between bulk modulus of M_2AC and MC configurations.

Elastic properties of these materials can be understood based on their electronic structure, which is readily available
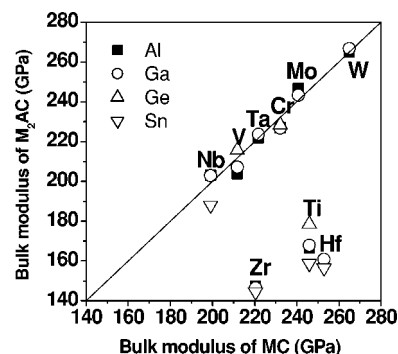

FIG. 1. The bulk moduli of M_2AC versus the bulk moduli of the corresponding MC, where M is a transition metal from group IVB, VB, and VIB, A is a IIIA and a IVA group element. Clearly, M_2AC phases can be classified into two groups: One inheriting the bulk modulus of the corresponding MC and the other with larger deviations.
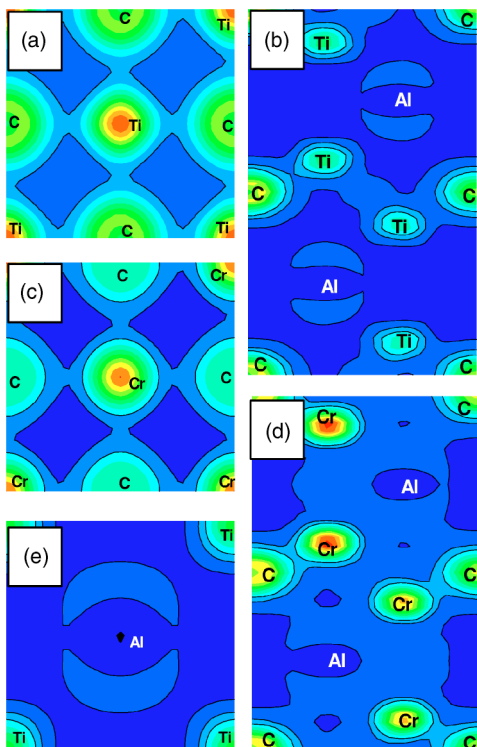
FIG. 2. (Color online) Charge-density contours for (a) TiC, (b) Ti_2AlC, (c) CrC, (d) Cr_2AlC, and (e) TiAl. These cuts are made in the $(11\bar{2}0)$ plane for the ternaries and in the (100) for the binaries, where the charge density varies from 0.2 (blue) to 2.4 $e/\text{Å}^3$ (dark red).

from the density-functional theory calculations carried out here. Figure 2 shows the charge-density contours in the $(11\bar{2}0)$ plane for Ti_2AlC [Fig. 2(b)] and Cr_2AlC [Fig. 2(d)] as well as in the (100) plane for TiC [Fig. 2(a)] and CrC [Fig. 2(c)], where the latter two phases crystallize in NaCl structure with space group $Fm\bar{3}m$. Analyzing the M-C bonding in TiC and CrC, it can be concluded that the bonding is characterized by covalent and ionic contributions and that this character is essentially conserved in the M_2AC ternaries. While the charge-density distribution of TiC is similar to the one of CrC, the charge distribution of the related ternaries shows extensive differences. The coupling between the MC layer and the Al layer is weaker for Ti_2AlC as compared to Cr_2AlC. In fact, the bonding between Ti and Al in Ti_2AlC is similar to the bonding in TiAl (space group $P4/mmm$), as can be seen in Fig. 2(e). On the other hand, the coupling between individual CrC layers in Cr_2AlC is similar to the Cr-C bond in CrC, see Fig. 2, even though CrC layers are interleaved with Al planes. Hence, the elasticity data presented in Fig. 1 can be understood based on the charge-density data discussed here. These findings provide a pathway for tailoring the elastic properties of M_2AC by tuning the valence electron population. As the valence electron population of the transition metal M is increased, more charge is placed in the M-C bonds, which is due to an increase in the C p-M d hybridization as can be seen in Fig. 3, where the partial density of states data are presented for Ti_2AlC [Fig. 3(a)], Cr_2AlC [Fig. 3(b)], and Cr_2GeC [Fig.
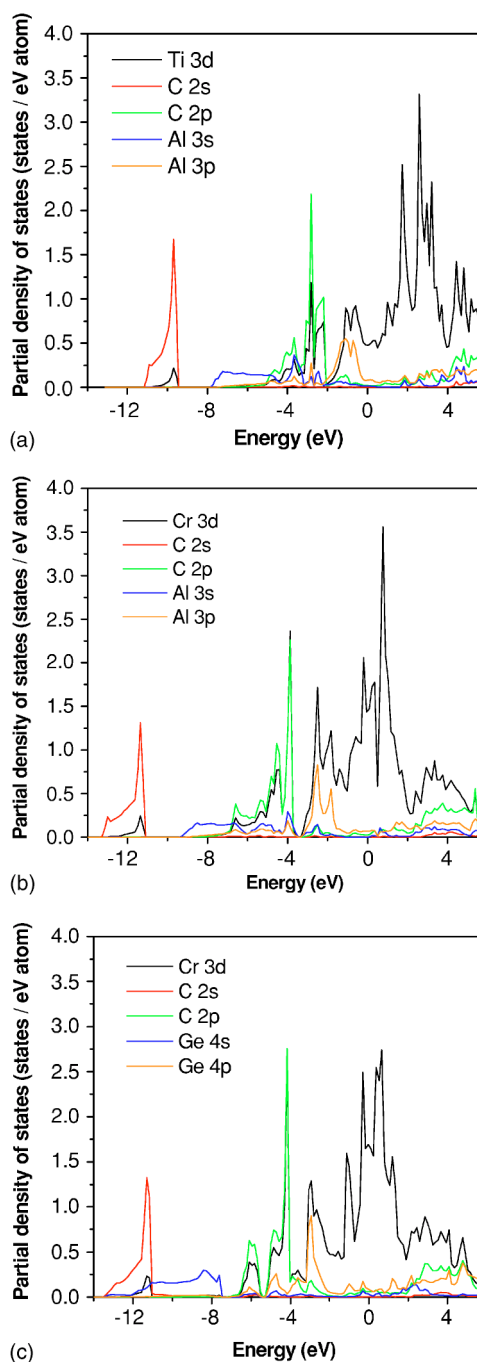

FIG. 3. (Color online) Partial density of states for (a) Ti_2AlC, (b) Cr_2AlC, and (c) Cr_2GeC. The Fermi energy is set to 0 eV. The major contribution to bonding stems from C $2p$-M $3d$ hybridized states. This in accordance with literature on carbides and nitrides (Refs. 33 and 34).

3(c)]. The hybridized C $2p$-M $3d$ states dominate the bonding in these demonstrating phases. Another difference in bonding between the Ti_2AlC and Cr_2AlC structures are the weakly hybridized A p-M d states which are very near to the Fermi level for Ti_2AlC and around -2 eV for Cr_2AlC. This indicates that the Ti-Al bond is indeed weaker than the Cr-Al bond. This agrees well with what we have observed for the

charge-density distribution in the $(11\bar{2}0)$ plane of Ti_2AlC and Cr_2AlC.

Utilizing an identical approach, we will now discuss the effect of A-element substitution. We have substituted Al in M_2AlC by Ga, Ge, and Sn and found that the substitution of the IIIA elements by IVA elements does not affect the elastic properties significantly. Based on our partial density of states data, we suggest that this behavior can be understood. We cannot identify any considerable differences in the dominating C p-M d hybridized states between Cr_2AlC and Cr_2GeC [see Figs. 3(b) and 3(c)]. The same holds for the Ti-and V-based sister compounds. The only difference that could be identified originates from the bonding within the A layer and the number of states at the Fermi energy (N_F). The $s-p$ hybridization in Ge layers decreases and the N_F is higher compared to Cr_2AlC, indicating that the one extra valence electron in Ge contributes to antibonding states. Furthermore, it is reasonable to assume that the role of the A element might be of similar nature in other $M_{n+1}AC_n$ with $n = 2$, assigning our discussions more general merits.

In summary, we have shown that by tuning the valence electron population of the transition metal M in M_2AC changes in the chemical bonding between the MC layers and the A layers can be induced. It is demonstrated that the bulk modulus of these materials can be varied from 145 to 272 GPa. Based on our calculations we suggest a classification of these materials into two groups: One group with strong coupling, where bonding and properties of the binary MC is conserved, and the group with weak coupling, where this is not observed. We have shown that this can be understood in terms of valence-electron-induced changes in coupling. These results may have implications for the understanding of properties, enabling the technological application of these fascinating ternary phases.

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