

General trend of the mechanical properties of the ternary carbides $M_3\text{SiC}_2$ (M =transition metal)

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We present results from first-principles calculations of ternary transition metal carbides in the $M_3\text{SiC}_2$ series (where M =early transition metal). We predict structural and mechanical properties of these new $M_{N+1}AX_N$ phases. The bulk modulus of the ternary carbides, $M_3\text{SiC}_2$, are in the calculations found to be proportional to the bulk modulus of the corresponding binary carbides, MC . We have analyzed this behavior using a simple, nearest-neighbor bond model, as well as from first-principles total energy calculations and have found that it is caused by a considerably weaker M -Si bond compared to the M -C bond.

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I. INTRODUCTION

In recent years, the ternary transition metal carbides and/or nitrides have become materials of intense research, especially the so-called MAX-phases; $M_{N+1}AX_N$, where M is an early transition metal, A an A-group element, and X is C and/or N.¹⁻³ The MAX materials have remarkable mechanical properties,⁴ exceptional shock resistance and damage tolerance,^{5,6} high loss factor,⁴ fully reversible plasticity,^{4,7} negligible thermopower, and high thermal conductivity, etc.^{4,8} Due to these unique properties, they have the potential for industrial applications. Ti_3SiC_2 is the prototype of the MAX compounds and has been investigated intensively.^{1,4-7} However, a lot of attention has also been paid to the M_2AX compounds.^{1,9-11} Recently Sun *et al.*¹⁰ analyzed the trend of the bulk modulus of the $M_2\text{AlC}$ (M =early 3d transition metals) series and found that the bulk modulus increases as the 3d series is traversed. They also studied the general trend of the bulk modulus of the $M_2\text{AC}$ compounds and found that the M =Ti, Zr, and Hf metal carbides were considerably different from the other MAX compounds.¹² In the M_3AX_2 series, only a few compounds have been studied experimentally or theoretically,^{1,13} with Ti_3SiC_2 being an exception to this fact. However, new members of the M_3AX_2 series are continuously being synthesized.¹⁴ A theoretical analysis for these new MAX phase materials is needed to understand their properties. In this paper, we report on theoretical predictions of structural and mechanical properties of the $M_3\text{SiC}_2$ (M =3d, 4d, and 5d transition metal) series using a first-principle method. The crystal structures of these predicted new MAX compounds are reported and the trend of the mechanical properties is analyzed.

II. DETAILS OF THEORETICAL CALCULATIONS

The calculations were performed using the VASP (Vienna *Ab initio* Simulation Program) code^{15,16} with the generalized-gradient approximation and projected-augmented wave potentials.^{17,18} It is worth noting that these calculations are typically made using the local density approximation (LDA) or generalized-gradient approximation (GGA), and here we have chosen the latter. The electronic wave functions were

sampled on a $12 \times 12 \times 4$, or 69 k -point mesh, and on a $24 \times 24 \times 24$, or 413 k -point mesh in the irreducible part of the Brillouin zone (BZ) (Ref. 19) for the MAX compounds, and the binary carbides with NaCl-type structure, respectively. For WC with a hexagonal lattice, a $24 \times 24 \times 24$, or 484 k -point mesh was employed in the BZ. The kinetic energy cutoff for the wave functions was 500 eV. The augmented cutoff energy was 604 eV. Convergence in the total energy with respect to the number of k points and the plane-wave cutoff has been checked carefully. Spin polarization was considered for the Cr compound. Full relaxation of both lattice parameters and the coordinates of the atoms was performed while the volume was kept fixed. The equilibrium volume and bulk modulus were calculated by a fit of the volume-energy curves using Murnaghan's equation of state.²⁰

III. RESULTS AND DISCUSSION

Most of the binary early transition metal carbides crystallize in the NaCl-type structure, except WC where a hexagonal structure type has been found.²¹⁻²³ The calculated lattice parameter and bulk modulus for these binary carbides are in good agreement with the experimental data and former theoretical calculations.²¹⁻²⁴ Table I lists the calculated results (lattice parameters, equilibrium volumes, internal structural parameters, c/a ratio, and bulk modulus) for the $M_3\text{SiC}_2$ compounds. As shown in Table I, the optimized lattice parameters for Ti_3SiC_2 are in good agreement with the experimental values,^{1,7} as well as previous calculations,^{24,25} which serves as a test of our computational technique. Note that the calculated bulk modulus to some extent depends on the computational method (i.e., if one is using the LDA or GGA, or if one uses projector-augmented waves,²⁶ full-potential linear muffin-tin orbital method,²⁷ or linear augmented plane waves²⁸), with a scatter in the calculated data of approximately 20%. The main cause of the scatter is due to the type of exchange-correlation functional chosen in the calculations. Since for the other compounds listed in Table I, no experimental data are available to compare with, these results can serve only as a prediction.

The Zr_3SiC_2 compound is predicted to have the largest volume in the series of $M_3\text{SiC}_2$ compounds (Table I). Fur-

TABLE I. The calculated results for the $M_3\text{SiC}_2$ (M =a transition metal) compounds using the density functional theory (DFT). $M_3\text{SiC}_2$ with space group $P6_3/mmc$ (No. 194 in the table), $M1$ at $2a(0,0,0)$, $M2$ at $4f(\frac{1}{3}, \frac{2}{3}, z_{M2})$, Si at $2b(0,0,\frac{1}{4})$ and C at $4f(\frac{1}{3}, \frac{2}{3}, z_C)$. The experimental data for Ti_3SiC_2 are included for comparison.

	c/a	z_{M2}	z_C	V (\AA^3)	B (GPa)
Ti_3SiC_2	5.7823	0.134	0.9279	146.80	187
	5.7811 (Ref. 7)	0.135	0.932 (Ref. 7)	143.50 (Ref. 7)	190 (Ref. 29) 206 (Ref. 31)
V_3SiC_2	6.0150	0.1318	0.9295	129.06	219
Cr_3SiC_2	5.8639	0.1307	0.9281	121.07	234
Zr_3SiC_2	5.5848	0.1399	0.9256	183.94	173
Nb_3SiC_2	5.9557	0.1358	0.9288	161.53	201
Mo_3SiC_2	5.8522	0.1377	0.9277	147.96	236
Hf_3SiC_2	5.6174	0.1377	0.9262	176.26	185
Ta_3SiC_2	6.0181	0.1358	0.9295	158.40	231
W_3SiC_2	5.9563	0.1347	0.9287	147.79	273

ther, the MAX compounds with $M=\text{V}$, Nb , and Ta , have larger c/a ratios than the others. Also the volumes of the $M_3\text{SiC}_2$ compounds decrease for M metals in the same row in the Periodic Table with increasing atomic number, while the bulk modulus shows a different behavior, since it increases with the increasing atomic number. The same type of behavior was found for the compounds in the $M_2\text{SiC}$ series.¹⁰ The calculated bulk modulus for Ti_3SiC_2 is ~ 187 GPa, in good agreement with the experimental data [190(± 10) GPa or 206 GPa],^{1,7,29,31} and the previous theoretical value (204 GPa), obtained from a LDA calculation.³⁰ Table I also shows that the bulk modulus increases from the Ti based system, $M=\text{Ti}$ (187 GPa) to $M=\text{V}$ (219 GPa) and to $M=\text{Cr}$ (234 GPa). This is also in agreement with the behavior of the $M_2\text{SiC}$ series.¹⁰ As shown in Fig. 1, the value of the bulk modulus of a ternary $M_3\text{SiC}_2$ compound is approximately $\frac{3}{4}$ of that of the corresponding binary transition metal carbide. Two ternary $4d$ metal based compounds ($M=\text{Nb}$ and Ta) have their bulk modulus somewhat under the $\frac{3}{4}$ line. We also note that Cr_3SiC_2 is the only magnetic compound in this series (it was treated as a ferromagnet in the calculations). The magnetic moment is calculated to be about $0.45 \mu_B/\text{Cr}$ atom at the equilibrium volume, and we find that the magnetic moment decreases slightly with pressure. The calculations also show that the unstable CrC compound with the NaCl-type structure does not order magnetically. The calculated bulk modulus of the Cr_3SiC_2 phase deviates the most from the $\frac{3}{4}$ line (see Fig. 1), which is likely to be caused by the magnetism in this system.

Figure 2 shows the compressibility of the a and c axis for Ti_3SiC_2 . At low pressure the c axis decreases nonlinearly and somewhat faster than the a axis. However, from a pressure larger than 40 GPa, the difference becomes small. Therefore, generally speaking this compound is isotropic, as argued by Ahuja *et al.*³⁰ This is somewhat surprising, since the crystal structure at the MAX phases has been seen as a layered nanolaminate.¹

As mentioned the $M_3\text{SiC}_2$ compounds can be regarded as layered materials. Along the c axis the structure is composed

of a pure Si layer sandwiched by a nearly close packed stacking of metal carbide ($M\text{-C-M-C-M}$) layers. Here, we carefully analyze the behavior of these crystals under pressure using Ti_3SiC_2 as a prototype. Along the c axis the structure consists of two types of slabs, the Ti-Si-Ti slab and the Ti-C-Ti-C-Ti slab. The thickness of these slabs is determined by the coordinates of the Ti_{II} atom, which is bonded to both Si and C atoms. The relative thickness of the Ti-Si-Ti slab is about 47% of the length of the c axis. As shown in Fig. 3, where the calculated pressure dependence on the slab thickness is shown, the Ti-Si-Ti slab is much softer relative to the Ti-C-Ti slab. This is due to the relatively weak bond between Ti-Si as compared to the Ti-C bond. In fact, if we investigate the calculated pressure dependence of the interatomic distances of the Ti-Si-Ti slab and the Ti-C-Ti slab separately, we find that the thickness of the Ti-C-Ti slab decreases only

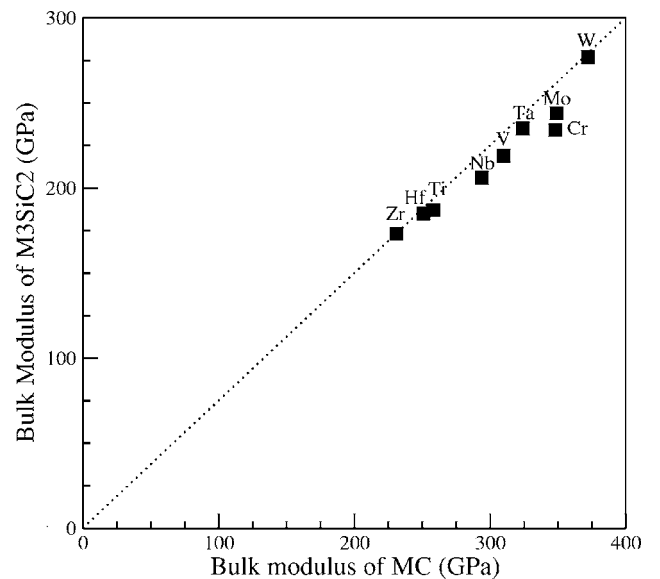


FIG. 1. The bulk moduli of $M_3\text{SiC}_2$ versus the bulk moduli of the corresponding MC , where M is a transition metal. The dotted line corresponds to the $\frac{3}{4}$ rule.

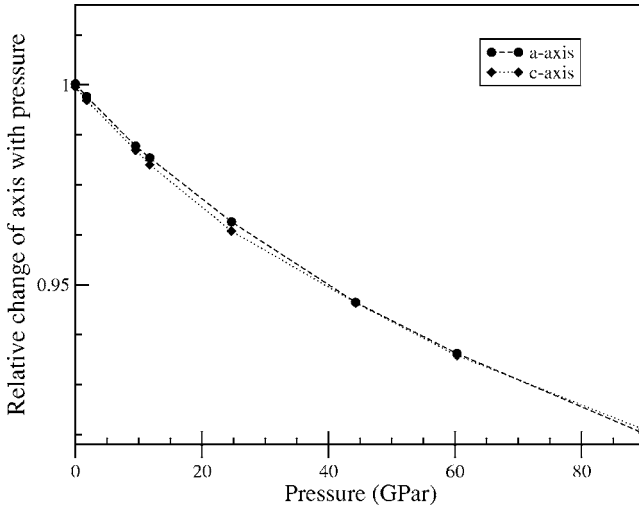


FIG. 2. The change of the relative lengths of the a and c axis for Ti_3SiC_2 with pressure. Clearly at low pressure the relative length of the c axis behaves nonlinearly and decreases faster than the a axis. It becomes more or less linearly for both the a and c axis at pressure above about 40 GPa.

slightly and almost linearly with pressures up to about 90 GPa. However, the pressure dependence of the interatomic distances of the Ti-Si-Ti slab is much stronger: at low pressure (0 to about 40 GPa) the thickness of the Ti-Si-Ti slab decreases rather strongly and nonlinearly, at a higher pressure (above about 40 GPa) it decreases slower and more linearly. Therefore, the observed nonlinear behavior of the compressibility of the c axis by Onodera *et al.*³¹ we conclude, is mainly caused by modifications of distances between planes in the Ti-Si-Ti slab.

To have a better understanding of the different strengths of the Ti-C and Ti-Si bonds, we have calculated the cleavage energies between different bonds along the (001) direction.

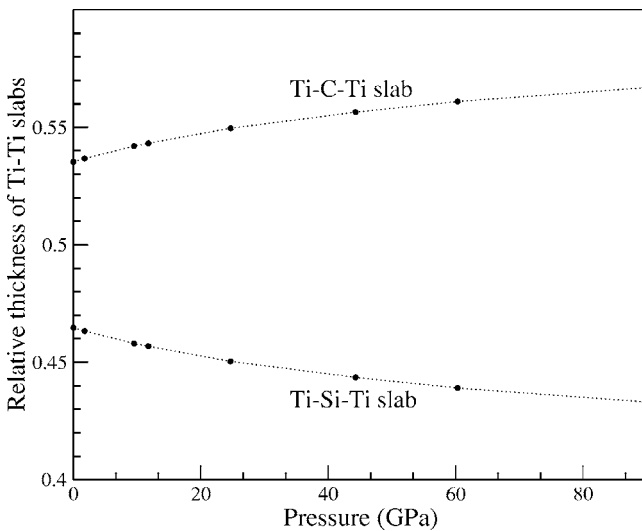


FIG. 3. The relative thickness of the Ti-C-Ti and Ti-Si-Ti slabs changes with pressure. Apparently with increasing pressure, the relative thickness of the Ti-Si-Ti slab decreases, while that of Ti-C-Ti slab increases.

TABLE II. The cleavage energy (J/m^2) along the (001) direction for Ti_3SiC_2 from first principles.

Ti-Si	$\text{Ti}_I\text{-C}$	$\text{Ti}_{II}\text{-C}$
1.58	3.08	3.58

There are three types of bonds that are relevant; $\text{Ti}_I\text{-C}$, $\text{Ti}_{II}\text{-C}$, and $\text{Ti}_{II}\text{-Si}$, and we calculated the total energy when these bonds are broken. This was done simply by separating, e.g., the distance between Ti_I and C to a sufficient large value so that the Ti-C bond is broken. The cleavage energies are then obtained by

$$E = (E_{\text{broken}} - E_{\text{bulk}})/2,$$

where E_{broken} is the total energy of the system with broken bonds. The calculated results are listed in Table II. As shown in Table II, the cleavage energy is about $3.08 \text{ J}/\text{m}^2$ for the system with broken $\text{Ti}_I\text{-C}$ bonds, and about $3.58 \text{ J}/\text{m}^2$ for the system with broken $\text{Ti}_{II}\text{-C}$ bonds. These data are very close to the calculated results for TiC [about $3.12 \text{ J}/\text{m}^2$ along the (111) surface].³² It is also clearly seen that the energy needed to break the Ti-C bonds is about two times of that of breaking the Ti-Si bonds.

The analysis of the section above suggested that the individual Ti-C bonds are modified only to a small extent when the Si layers are present in the MAX phase. This motivates an analysis based on the tight-binding, nearest-neighbor theory and below we present a simple model based on this. Hence, we proceed with a simple model where the energy of the bonds between Ti and C planes is written as $E = K_1(d^I - d_0^I)^2$, where d_0^I is the equilibrium distance between Ti and C planes and K_1 is a force constant. The energy of the binding between Ti and Si planes is written in a similar way as $E = K_2(d^{II} - d_0^{II})^2$, where d_0^{II} is the equilibrium distance between Ti and Si planes. This form of the bond energy is consistent with the elastic response of materials, in general.^{33,34} No other contributions are considered in this simple model, since as pointed out by Ahuja *et al.*³⁰ these systems are rather isotropic when it comes to the bulk modulus and for this reason an analysis based on interactions in one dimension suffices. A conventional unit cell of Ti_3SiC_2 contains eight Ti-C bonds and four Ti-Si bonds, which with the simplifying assumption that $d_0^I = d_0^{II}$, gives $E_{\text{MAX}} = 8K_1(d - d_0)^2 + 4K_2(d - d_0)^2$ (where the superscripts I and II have been dropped). A similar expression can be obtained for TiC by replacing the four Ti-Si bonds with Ti-C bonds and we obtain in this case $E_{\text{TiC}} = 12K_1(d - d_0)^2$. With this simple model the bulk modulus can be calculated analytically and we obtain a ratio between the bulk modulus of the MAX phase to that of TiC as $B_{\text{MAX}}/B_{\text{TiC}} = \frac{2}{3} + K_2/3K_1$. We can now identify a criterion between the force constants, K_1 and K_2 , for when the ratio $B_{\text{MAX}}/B_{\text{TiC}}$ should equal $\frac{3}{4}$, and this criterion is $K_1 = 4K_2$, in other words the Ti-C bonds should have a force constant four times stronger than that of the Ti-Si bonds. In order to check the validity of this simple analysis we performed a first-principles calculation of the total energy versus strain along the c axis— S (S can be calculated from

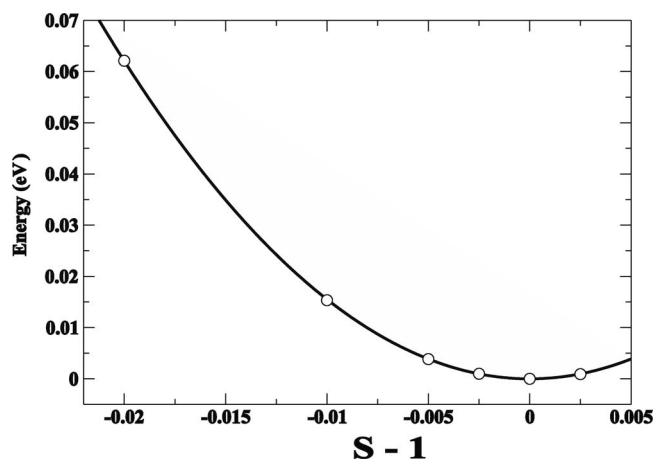


FIG. 4. Calculated energy vs strain (S , as given by, e.g., c/c_0) for Ti_3SiC_2 (open circles) and the fit using $E=K^*S^2$ (solid line).

c/c_0 , where c_0 is the length of the c axis at equilibrium). In Fig. 4 we show the first-principles energy versus strain. The calculated energy points are compared to the simple expression of the total energy discussed above, using $K_1=4K_2$, which results in an expression $E_{\text{MAX}}=9K_1S^2$. It may be noted that the simple model follows the first-principles data quite closely.

It is important to realize that although the calculated cleavage energies suggest a Ti-C bond that is twice as strong as the Ti-Si bond, the force constants determined in our simple model, which describes the elastic response for small modifications in the atomic positions, does not have to scale accordingly. Hence, our analysis of the force constants being four times stronger for Ti-C bonds is not inconsistent with the data presented in Table II. Let us end this section with a comment on the bonds of transition metal carbides and silicides in general. As we move from early transition metals

(e.g., Ti) towards the heavy elements the M -C bond is weakened whereas the M -Si bond is strengthened.^{22,23} In our simple model presented above this shows up in an increase of the K_2/K_1 ratio. If this ratio is increased from $\frac{1}{4}$ (the value for Ti_3SiC_2) to a value that is $\sim 10\%$ larger (this could potentially be the case for V_3SiC_2) we obtain a ratio $B_{\text{MAX}}/B_{\text{VC}}=0.76$, i.e., a value quite close to the data presented in Fig. 1. One can continue this analysis by comparing a calculated bulk modulus for a series of MAX phases with different composition, e.g., the $\text{Ti}_{n+m}\text{Si}_n\text{C}_m$ series, where n and m are integer values between 1 and 7.³⁵ In Ref. 35 we showed that the bulk modulus decays linearly with the ratio between the number of Si layers to the number of Ti layers, and this behavior is precisely what our simple model gives. This analysis, of course, relies on the fact that the strength between Ti and Si atoms and between Ti and C atoms is independent of the values of n and m . As a result of the total energy analysis in Ref. 35, as well as from the argument from the tight-binding theory, it was indeed concluded that this is the case.

In summary, using a first-principles method, we have predicted the structure and mechanical properties of a series of new $M_3\text{SiC}_2$ phases. The bulk moduli of these ternary carbides are approximately $\frac{3}{4}$ of those of their corresponding binary carbides, and using a simple model this is explained by a four times stronger Ti-C bond compared to the Ti-Si force constant. Our predictions for new MAX phases will hopefully motivate further experimental work on these materials.

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