



# First principles study the stability, mechanical and electronic properties of manganese carbides



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## ABSTRACT

The stability, elasticity, hardness and electronic properties of Mn–C binary compounds are investigated by first principles calculations. The lattice parameters, cohesive energy and formation enthalpy of these compounds are calculated and discussed. Furthermore, the elastic constants are calculated by the stress–strain method and satisfy the Born–Huang's criterion. Meanwhile, the Voigt–Reuss–Hill approximation is applied to estimate the elastic moduli. Besides, the mechanical anisotropy of these compounds is studied by the anisotropic indexes and plotting 3D surface contour of Young's modulus. A semi-experience method is used to evaluate the hardness of these carbides. Moreover, the sound velocity and Debye temperatures of Mn–C compounds are also discussed.

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## 1. Introduction

In recent decades, transition metal carbides have been widely studied and applied in the heat-resistant and hard materials industries owe to their outstanding mechanical properties and chemical stability, such as high melting point, extreme hardness and high thermal conductivity. The precipitation of transition metal carbides in steels can dramatically influence the mechanical properties of the steels. Generally, the mechanical properties are related to the components, crystal structure, thermodynamic and mechanical properties of transition metal carbides. Manganese is a common alloying element used in steel and it can react with carbon to form the Mn–C carbides, i.e. Mn<sub>3</sub>C, Mn<sub>5</sub>C<sub>2</sub>, Mn<sub>7</sub>C<sub>3</sub> and Mn<sub>23</sub>C<sub>6</sub>. Some manganese carbides have been investigated by theory and experiments. Karen et al. [1] synthesized the pure compounds of Mn<sub>5</sub>C<sub>2</sub>, Mn<sub>7</sub>C<sub>3</sub> and Mn<sub>23</sub>C<sub>6</sub> and studied the crystal structures, bonding features and magnetic properties. They found that Mn<sub>23</sub>C<sub>6</sub> is magnetically ordered below 104 K. Southard and Moore [2] made contributions to disclose the enthalpy of Mn<sub>3</sub>C from room temperature to 1140 °C and show the phase transition at 1037 °C. Myers and Fishel [3] prepared the Mn<sub>3</sub>C by aluminothermic reduction method and investigated its hydrolysis with water and acids. Xie et al. [4,5] calculated the lattice parameters and cohesive energy for Mn<sub>7</sub>C<sub>3</sub> and Mn<sub>23</sub>C<sub>6</sub> that the results were

in good agreement with the experimental data. Djurovic et al. [6] assessed the Mn–C system by means of the CALPHAD method and *ab initio* calculations to obtain the lattice parameters and formation enthalpy, which was helpful to modify the Mn–C phase diagram. However, the mechanical and electronic properties of Mn–C compounds are rarely reported and the elastic anisotropy of these compounds has not yet been discussed systematically in the literature so far.

In this work, the first principles calculations are employed to investigate systematically the stability, chemical bonding characteristics, mechanical properties and Debye temperature of Mn–C binary compounds. The obtained values of various properties are compared with the available theoretical and experimental results.

## 2. Calculation methods and models

The crystal structures of manganese carbides are shown in Fig. 1. Mn<sub>3</sub>C, Mn<sub>5</sub>C<sub>2</sub>, Mn<sub>7</sub>C<sub>3</sub> and Mn<sub>23</sub>C<sub>6</sub> carbides were calculated by density functional theory (DFT) as implemented in Cambridge Sequential Total Energy Package (CASTEP) code [7,8]. The interactions between ionic cores and valence electrons were represented by ultra-soft pseudo potentials. For Mn and C, the valence electrons considered are 3s<sup>2</sup>3p<sup>6</sup>3d<sup>5</sup>4s<sup>2</sup> and 2s<sup>2</sup>2p<sup>2</sup>, respectively. The calculations in the first irreducible Brillouin zone were conducted with a 8 × 8 × 8 *k* point mesh using Monkhorst–Pack scheme [9]. Generalized gradient approximation (GGA) of PBE approach was used for exchange–correlation energy calculations [10]. A kinetic energy

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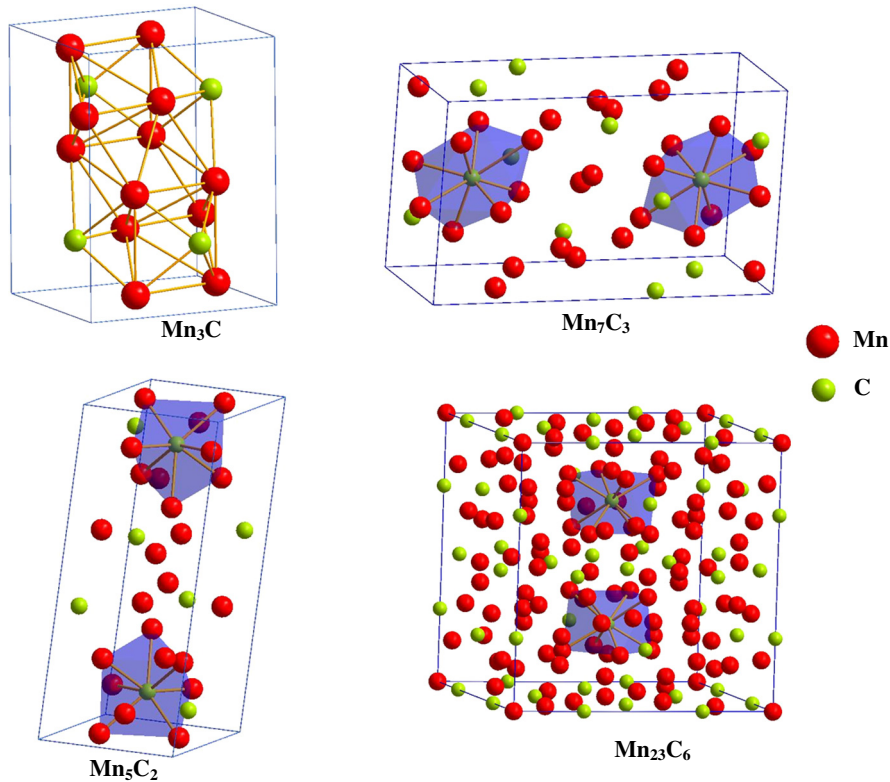


Fig. 1. The crystal structures of  $\text{Mn}_3\text{C}$ ,  $\text{Mn}_5\text{C}_2$ ,  $\text{Mn}_7\text{C}_3$  and  $\text{Mn}_{23}\text{C}_6$ .

cut-off value of 450 eV was used for plane wave expansions. Broyden–Fletcher–Goldfarb–Shannon (BFGS) optimization method was applied to obtain the equilibrium crystal structures of carbides. The total energy changes during the optimization process were finally converged to  $2 \times 10^{-6}$  eV and the forces per atom were reduced to 0.05 eV/Å.

In order to investigate the chemical stability of these compounds, the cohesive energy and formation enthalpy were calculated within the following equations:

$$E_{\text{coh}}(\text{Mn}_x\text{C}_y) = E_{\text{tot}}(\text{Mn}_x\text{C}_y) - xE_{\text{iso}}(\text{Mn}) - yE_{\text{iso}}(\text{C}) \quad (1)$$

$$\Delta_f H(\text{Mn}_x\text{C}_y) = E_{\text{coh}}(\text{Mn}_x\text{C}_y) - xE_{\text{coh}}(\text{Mn}) - yE_{\text{coh}}(\text{C}) \quad (2)$$

where  $E_{\text{coh}}(\text{Mn}_x\text{C}_y)$  and  $\Delta_f H(\text{Mn}_x\text{C}_y)$  are the cohesive energy and formation enthalpy of manganese carbides, respectively;  $E_{\text{tot}}(\text{Mn}_x\text{C}_y)$  is the total energy of  $\text{Mn}_x\text{C}_y$  phase;  $E_{\text{iso}}(\text{Mn})$  is the total energy of a single Mn atom;  $E_{\text{iso}}(\text{C})$  is the total energy of a single C atom;  $E_{\text{coh}}(\text{Mn})$  is the cohesive energy of pure  $\alpha$ -Mn and  $E_{\text{coh}}(\text{C})$  is the cohesive energy of graphite.

### 3. Results and discussion

#### 3.1. Stability

The cell parameters, cohesive energy and formation enthalpy of manganese carbides are given in Table 1. The calculated lattice parameters in this work are in good agreement with the experimental values [1,11] and other calculated results [6]. Furthermore, the average deviation of our results to experimental results for lattice parameters is less than 3%, which can be attributed to the approximation method in the work and thermodynamic effects on the crystal structures. The cohesive energy and formation enthalpy are used to determine the relative stability of these Mn–C compounds. As defined in Eqs. (1) and (2), the smaller the negative

values of these two thermodynamic parameters, the more stable the compound. The cohesive energy values of  $\text{Mn}_3\text{C}$ ,  $\text{Mn}_5\text{C}_2$ ,  $\text{Mn}_7\text{C}_3$  and  $\text{Mn}_{23}\text{C}_6$  are  $-9.302$ ,  $-9.277$ ,  $-9.283$  and  $-9.295$  eV/atom, respectively, and the formation enthalpy values of  $\text{Mn}_3\text{C}$ ,  $\text{Mn}_5\text{C}_2$ ,  $\text{Mn}_7\text{C}_3$  and  $\text{Mn}_{23}\text{C}_6$  are  $-0.042$ ,  $-0.018$ ,  $-0.030$  and  $-0.033$  eV/atom, respectively, indicating that they are thermodynamically stable. The stability sequence of these Mn–C compounds follows the order:  $\text{Mn}_3\text{C} > \text{Mn}_{23}\text{C}_6 > \text{Mn}_7\text{C}_3 > \text{Mn}_5\text{C}_2$ , which is consistent with the results obtained by Djurovic et al. [6]. Therefore, it is evidence that  $\text{Mn}_3\text{C}$  is the most stable structure among them, and  $\text{Mn}_3\text{C}$  shows the smaller negative cohesive energy and formation enthalpy value.

#### 3.2. Electronic structures

The electronic structure and chemical bonding characteristics of the manganese carbides can be discussed by means of partial density of states, Mulliken population analysis and metallicity. Fig. 2 depicts the calculated total density of states (TDOS) and partial density of states (PDOS) of the Mn–C compounds. The DOS values at the Fermi level are greater than zero, indicating the metallicity of electronic conductivity of  $\text{Mn}_3\text{C}$ ,  $\text{Mn}_5\text{C}_2$ ,  $\text{Mn}_7\text{C}_3$  and  $\text{Mn}_{23}\text{C}_6$ . Moreover, it is observed that the valence band from  $-15$  eV to  $-11$  eV is mainly determined by the C–p bands. The band extending from  $-8$  eV to  $2$  eV is composed of C–p, Mn–p and Mn–d bands and the contribution from Mn–p is low near the Fermi level for all the manganese carbides, which shows p–d hybridization between C and Mn atoms formed covalent bonding. Nevertheless, the center of gravity of C–p bands does not completely coincide with the Mn–d bands, implying ionic interaction in these compounds [13].

Mulliken population analysis is one parameter to reveal chemical bonding characteristics and the results are listed in Table 2. We used Eqs. (3) and (4) to calculate the average bond length and overlap population:

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