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Structural, mechanical, dynamical and electronic properties and high-pressure behavior of Mo_2GeC: A first-principles study

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ABSTRACT

The structural, mechanical, dynamical and electronic properties of ternary MAX phase Mo_2GeC under high pressure has been investigated by first-principles calculations within the generalized gradient approximation of density functional theory. The structural parameters in the pressure range of 0–50 GPa are presented and it is found that Mo_2GeC is much more compressible along the *a* direction than along the *c* direction. Moreover, mechanical properties including elastic constants, elastic moduli, Possion's ratio, Vickers hardness, and Deybe's temperature are given. We find that C_{33} increases rapidly as pressure is increased, which implies a strong resistance to the compression strain along the *c* direction. This mechanical anisotropy is also illustrated by the directional bulk modulus. Furthermore, Mo_2GeC is dynamically stable from 0 to 50 GPa by the phonon calculation. Finally our electronic structure calculation shows that Mo_2GeC is predicted to be metallic and the metallicity of Mo_2GeC increases with increasing pressure. The charge density distributions show the existence of the covalent Mo—C bonds and with increasing pressure, the covalent Mo—Ge bonds and the covalent Mo-Mo bonds. Bader's charge analysis shows that the Mo charges increase while the Ge and C charges decrease as pressure is increased.

1. Introduction

Two decades ago, Barsoum and co-workers reported their pioneering work on bulk Ti_3SiC_2 [1] and then found this compound could be classified as derivatives of the so-called H-phases [2], most already discovered and produced in powder form in 1960s by Nowotny's group [3]. Barsoum's work stimulated a tremendous progress in the synthesis of this new class of compound and now all these compounds were called $M_{n+1}AX_n$ (MAX) phase [4], where $n = 1, 2$ or 3, M is an early transition metal, A is an A-group element (mostly IIIA and IVA) and X is C or N.

Different from the other materials, MAX phases combine many of the best attributes of metals and ceramics [2], such as easily machinable, excellent electric and thermal conductor, good oxidation resistance and high stiffness. These unique and extraordinary properties enable MAX phases to be the promising candidate materials for applications in diverse fields. So in recent years, there are many theoretical [5–7] and experimental [1,8] researches on MAX phases.

MAX phase is layered and hexagonal with $M_{n+1}X_n$ layers interleaved with layers of pure A (see Fig. 1 as an example). The removal of the 'A' layer from MAX phases results in two-dimensional (2D) carbide or nitride nanosheets, which are called MXenes [9,10]. Recently the two-dimensional Mo_2C has been proposed to be a potential thermoelectric materials for energy-related applications [11], and then synthesized and characterized by Barsoum's group [12]. This Mo_2C MXene indeed behaves as a semiconductor and performs well when tested as an electrode material for Li-ions [12]. The technological progresses make the 2D Mo_2C and corresponding Mo_2AC as the cutting-edge research of the MAX phases.

Among the Mo_2AC MAX phases, Mo_2GaC has already been synthesized in 1960s [4,13] and recently Mo_2AlC has also been synthesized as a solid solution [8]. As concern the theoretical researches, computational modeling and simulation, especially the first principles density functional theory (DFT) [14,15] calculations, have already provided useful information about MAX phases at the atomic scale and the macroscopic scale. For Mo_2AC MAX phases, Shein et al. [7,16] calculated the structural, elastic, electronic properties of Mo_2GaC, Ghebouli et al. [17] investigated the structural, elastic and thermal properties of M_2SiC MAX phases including Mo_2SiC, and Bai et al. [18] studied the lattice dynamics of Al-containing MAX phases including Mo_2AlC. In addition, Emmerlich et al. [19] systematically study the pressure dependence of M_2AlC including Mo_2AlC, and Gao et al. [20] calculated the mechanical properties of Mo_2GaC and found the extraordinary

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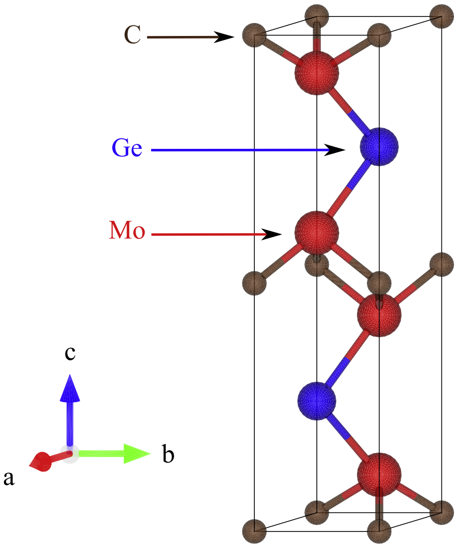

Fig. 1. Crystal structure of layered Mo_2GeC compound.

structural evolution. In particular, Khazaei et al. [21] computed the electronic structures and elastic properties of Mo_2AC MAX phases to study the effect of the interlayer element on the exfoliation of layered Mo_2AC. As illustrated above, most of the researches focused on the properties of Mo_2GaC and Mo_2AlC MAX phases under ambient pressure.

However, the considerable works have been devoted to understanding the compression behavior of MAX phase under high pressure. For example, Manoun and co-workers have reported a series of work on the compression behavior of M_2AlC (M = Ti, V, Cr, Nb, and Ta), M_2InC (M = Ti, $Ti_{0.5}Zr_{0.5}$), M_2SnC (M = Ti, Nb, Hf), M_2GaN (M = Cr, Ti), Ti_3AC_2 (A = Si, Ge, $Si_{0.5}Ge_{0.5}$, and $Al_{0.8}Sn_{0.2}$), and M_4AlX_3 (M = Ti, Ta) at pressure up to 50 GPa [22–31]. In particular, we are not aware of any theoretical work on Mo_2GeC under high pressure. Therefore, in this paper, our motivations are to study the structural, electronic, mechanical and dynamical properties of Mo_2GeC under high pressure. The reminder of this paper is organized as follows. Section 2 describes the computational methods and details. The results are given and discussed in Section 3 and a brief summary is presented in Section 4.

2. Computational methods and details

The first-principles DFT calculations are performed using VASP [32]. For the exchange-correlation potential, the generalized gradient approximation (GGA) using Perdew-Becke-Ernzerhof (PBE) [33] function is employed. The projector augmented wave (PAW) [34,35] pseudopotentials for Mo, Ge, and C $4p^6 5s^1 4d^5$, $3d^{10} 4s^2 4p^2$, and $2s^2 2p^2$ valence electronic configurations are chosen. The kinetic energy cutoff is taken as 650 eV and the $13 \times 13 \times 9$ k point meshes based on Monkhorst-Pack scheme [36] are adopted. In order to determine the partial occupancies for each Kohn-Sham orbitals, Methfessel-Paxton [37] smearing method with a width of 0.1 eV is used.

The theoretical crystal structure at different pressure is obtained from the structural relaxation that not only relaxes the ions but also allows the cell volume and shape to change. The total energy is minimized using the conjugate gradient and quasi-Newton algorithm until the force convergence reaches 0.005 eV/Å.

Here we must emphasize that the possible effect of strong correlated d electrons of the Mo atom is considered here. We use the popular GGA + U method [38,39] with $U = 4$ and $J = 0$ to calculate the optimized lattice parameters and bulk properties and find that the changes are negligible. Therefore most of the following calculations will adopt the pure GGA. The mechanical properties for the MAX crystal are described by the elastic tensor, which is the coefficient relates the stress tensor to the strain tensor in the general Hooke's law. Here the elastic tensor is also derived from the strain-stress relationship [40] by performing the finite distortion of the lattice, as implemented in VASP. For the elastic tensor of a hexagonal crystal, there are only five independent elastic constants, i.e., C_{11}, C_{12}, C_{13}, C_{33} and C_{44}.

For polycrystalline materials, the mechanical properties are usually described by various elastic moduli including bulk modulus B, shear modulus G, and Young's modulus E, which are the measure of the compressibility, rigidity, and stiffness. This moduli could be evaluated using the Voigt-Reuss-Hill approximation [41], in which the effective moduli is approximated by the arithmetic mean of the two well-known bounds for monocrystals according to Voigt [42] and Reuss and Angew [43]. For a hexagonal system, the formulation is given as:

$$B = \frac{B_V + B_R}{2}, \quad G = \frac{G_V + G_R}{2} \tag{1}$$

in which

$$B_V = \frac{2C_{11} + 2C_{12} + 4C_{13} + C_{33}}{9} \tag{2}$$

$$G_V = \frac{2C_{11} - C_{12} - 2C_{13} + C_{33} + 6C_{44} + 3C_{66}}{15} \tag{3}$$

$$B_R = \frac{1}{2S_{11} + 2S_{12} + 4S_{13} + S_{33}} \tag{4}$$

$$G_R = \frac{15}{8S_{11} - 4S_{12} - 8S_{13} + 4S_{33} + 6S_{44} + 3S_{66}} \tag{5}$$

with $S_{ij} = C_{ij}^{-1}$ being the elastic compliance tensor and $C_{66} = (C_{11} - C_{12})/2$.

In addition, Pugh's modulus ratio κ, Young's modulus E and Possion's ratio ν is given by:

$$\kappa = \frac{G}{B} \tag{6}$$

$$E = \frac{9BG}{3B + G} \tag{7}$$

$$\nu = \frac{3B - 2G}{6B + 2G} \tag{8}$$

Furthermore, Debye's temperature Θ_D is one of the simplest and most useful parameters to understand the thermodynamics properties of the materials and also a measure of the hardness [44]. It could be defined by:

$$\Theta_D = \frac{h}{k_B}\left[\frac{9n}{4\pi V_0}\right]^{1/3}\left[2\left(\frac{\rho}{G}\right)^{3/2} + \left(\frac{3\rho}{3B + 4G}\right)^{3/2}\right]^{-1/3} \tag{9}$$

where h and k_B are Planck and Boltzmann constants, respectively, n is the number of atoms in one formula unit, V_0 is the volume per formula unit, ρ is the mass density.

In order to study the mechanical anisotropy of the hexagonal MAX crystal, the directional bulk modulus along the a, b, c axes can be used, and they are given by the following equations [45]:

$$B_a = \frac{\Lambda}{2 + \alpha}, \quad B_b = B_a, \quad B_c = \frac{\Lambda}{2\alpha + \alpha^2} \tag{10}$$

in which

$$\Lambda = 2(C_{11} + C_{12}) + 4C_{13}\alpha + C_{33}\alpha^2 \tag{11}$$

$$\alpha = \frac{C_{11} + C_{12} - 2C_{13}}{C_{33} - C_{13}} \tag{12}$$