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Structural stability, electronic, mechanical and superconducting properties of CrC and MoC

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HIGHLIGHTS

- Electronic and mechanical properties of CrC and MoC are investigated.
- Pressure induced structural phase transition is predicted at high pressure.
- Electronic structure reveals that these materials exhibit metallic behaviour.
- Debye temperature values are computed for CrC and MoC.
- Superconducting transition temperature values are computed.

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ABSTRACT

The structural, electronic, mechanical and superconducting properties of chromium carbide (CrC) and molybdenum carbide (MoC) are investigated using first principles calculations based on density functional theory (DFT). The computed ground state properties like equilibrium lattice constants and cell volume are in good agreement with available theoretical and experimental data. A pressure induced structural phase transition from tungsten carbide phase (WC) to zinc blende phase (ZB) and then zinc blende phase (ZB) to nickel arsenide phase (NiAs) are observed in both chromium and molybdenum carbides. Electronic structure reveals that these carbides are metallic at ambient condition. All the calculated elastic constants obey the Born–Huang stability criteria, suggesting that they are mechanically stable at normal and high pressure. The super conducting transition temperatures for CrC and MoC in WC phase are found to be 31.12 K and 17.14 K respectively at normal pressure.

1. Introduction

Transition metal carbides have attracted much attention due to their excellent physical and chemical properties such as extreme stiffness, corrosion resistance, chemical inertness and catalytic behaviour. Chromium carbide is an extremely hard material with high corrosion resistance. Molybdenum carbides have many interesting properties such as high hardness and high catalytic activity [1]. Zhukov et al. [2] studied the electronic structure of CrC. A metastable NaCl structured CrC was formed by carbon ion implantation into pure chromium metal films at 50 KeV and the lattice constant was determined as 0.403 nm which was found to be stable only up to a temperature of 250 °C [3]. Singh and Klein [4] investigated the electronic structure and bulk modulus of CrC using the linearized augmented plane-wave method. Isaev et al. [5] computed the bulk modulus for NaCl phase of CrC and MoC as 322 GPa and 337 GPa respectively using density functional calculation. Grossman et al. [6] analysed the electronic and structural properties of transition metal carbides and nitrides. Jiang [7] investigated the structural, elastic and electronic properties of chromium mono carbide with tungsten carbide phase. Guillermet et al. [8] studied the cohesive properties of 4d transition metal carbides and nitrides in NaCl structure. The electronic structure and superconductivity of CrC were reported by Tutuncii et al. [9] in rock salt and tungsten carbide (WC) phases. They have reported that WC phase of CrC is more stable than rock salt phase. The superconducting transition temperature was estimated in the range of 25–35 K. Liu and Rodriguez [10] reported the catalytic properties of molybdenum carbide. Clougherty et al. [11] synthesised

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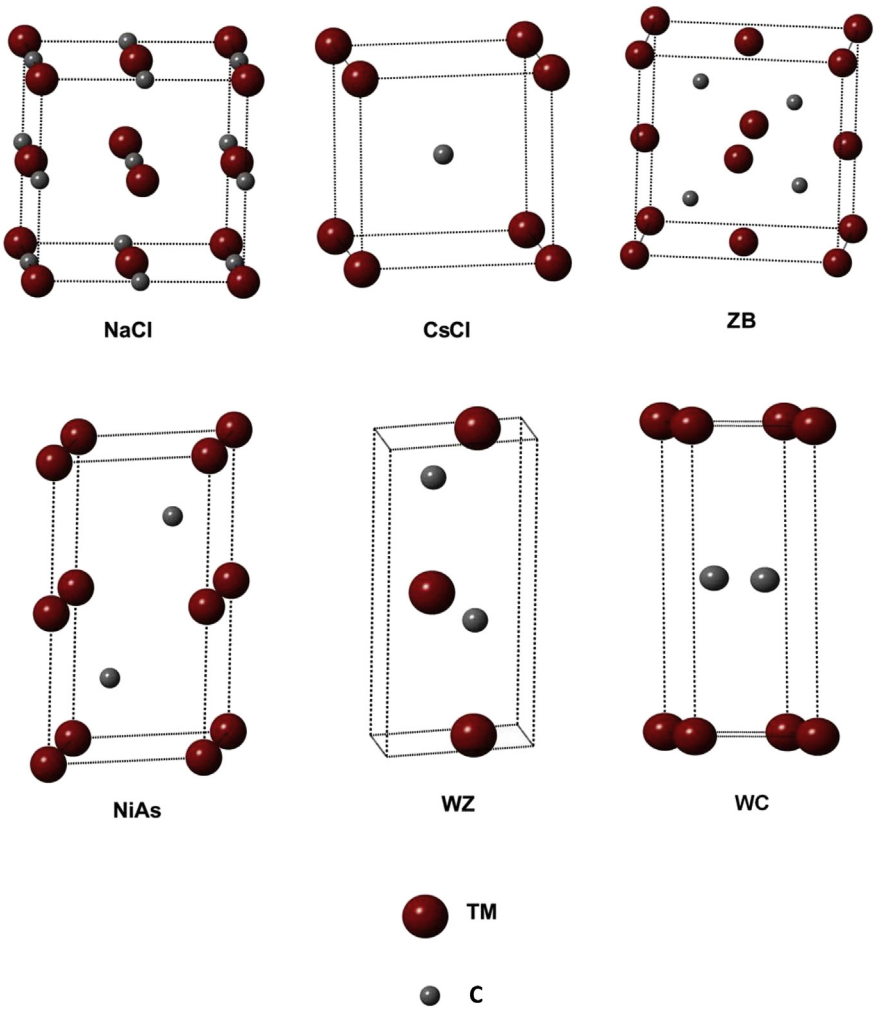

Fig. 1. Crystal structure of different phases of transition metal nitrides CrC and MoC.

molybdenum carbide in face centered cubic phase and other three hexagonal phases at various pressures. Liu et al. [12] have investigated crystal structure, electronic properties and hardness of MoC in different phases, namely, cubic-space group Fm3m (α−phase), hexagonal-space group − P6m2 (β−phase) and $p6_3/mmc$ (γ−phase). The Young's modulus values of α-MoC, β-MoC and γ-MoC were obtained as 395.5 GPa, 551.2 GPa, 399.5 GPa respectively. The Debye temperature and Gruneisen parameter were estimated for CrC and MoC by Krasnenko and Brik [13]. Zaoui et al. [14] analysed the electronic structure and the chemical bonding mechanism in MoC and they have found that the charge transfer from metal to non-metal atoms has the great influence on the bonding nature of MoC. The superconducting property of cubic $MoC_{0.681}$ were analysed experimentally and the superconducting transition temperature of $MoC_{0.681}$ is reported as 12 K [15]. Willens et al. [16] synthesised NbC, TaC, WC, and MoC in rock salt structure and the superconducting transition temperature of MoC was computed as 14.3 K.The structural stability, elastic and electronic properties of 5d mono carbides were investigated using full potential linear muffin tin orbital method [17].

In this paper, the structural, electronic, mechanical and superconducting properties of CrC and MoC are analysed. In particular, the elastic constants, Young's modulus, bulk modulus, shear modulus, Poisson's ratio, Lame's constants, Kleinman parameter, Zener isotropy and microhardness parameter are calculated to investigate the mechanical stability of chromium carbide and molybdenum carbide.

2. Theoretical framework

The *ab initio* calculations are performed within the generalized gradient approximation (GGA) [18–20] and local density approximation (LDA) [21] to the density functional theory using VASP code [22,23]. The interaction between the ion and electron is described by the projector augmented wave method [24]. Ground state geometries are determined by minimizing stresses and Hellman–Feynman forces using the conjugate-gradient algorithm with force convergence less than 10^{-3} eV/Å. Brillouin zone integration is performed with a Gaussian broadening of 0.1 eV during all relaxations. The Kohn–Sham orbitals are expanded using the plane wave cut-off energy of 600 eV. For accurate Brillouin zone integration, Monkhorst-Pack K-point mesh [25] with a grid size of 12 × 12 × 12 is used for structural optimization and total energy calculation. Iterative relaxation of atomic positions is stopped when the change in total energy between successive steps is less than 1 meV/cell. The valence electron configurations are Cr 3d5 4s1, Mo 4d5 5s1 and C $2s^2$ $2p^2$atoms.

The tight binding linear muffin tin orbital method [26–30] is used for the estimation of electron-phonon coupling constant (λ) and electron–electron interaction parameter (μ^*). This method