DIADEM - Bourse de Master - 2026/2027

Machine learning assisted crystal structure prediction of transition-metal hemicarbides (M_2C)

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Project Description

Transition-metal carbides have attracted renewed interest owing to their exceptional properties with broad potential applications, spanning refractory and hard materials, superconductivity and HER/OER electrocatalysis [1]. These materials uniquely combine ceramic hardness, thermal and chemical stability with metallic conductivity. The origin of their multifunctional properties can be traced down to the intricate interplay between metallic and covalent bonding, which governs their structural, electronic and mechanical behaviour [2, 3].

Among different metal-to-carbon stoichiometries, metal mono-carbides (MC) and metal hemicarbides (M_2C) have been extensively studied in 1970s and 1980s with particular emphasis on understanding of their crystal structure, phase diagram and optimization of synthesis routes [4, 5]. Structurally, these systems can be described as the combination of a metal sublattice forming an underlying core framework with occupation of the interstitial voids by the relatively small C atoms. Experimental reports establish that the metal sublattice in MC compounds primarily adapt FCC-derived arrangement with C atoms filling all the octahedral interstitial sites. The ordered occupation of the octahedral sites gives rise to the characteristic rosk-salt structure, in which the metal and carbon atoms form two interpenetrating FCC sublattices. In case of larger metal ions, the MC compound adapts hexagonal (AA stacking) arrangement [6]. Recently, high entropy carbides stabilizing in rock-salt phase have been reported [7]. Thus, the structural chemistry of MC systems is comparatively well established.

On the contrary, the M_2C systems are characterized by HCP-derived metal sublattice framework with partial occupation of the interstitial voids by the C atoms. The low carbon content with respect to the total number of available interstitial voids naturally leads to additional degrees of freedom associated with different degree of C/vacancy ordering [4, 5]. Furthermore, variations in the size and electronic configuration of the metal atoms, along with the differences in M-C bonding interactions promotes distortions of the metal framework and heterogeneity in local-atomic arrangements. Consequently, this combination of structural features gives rise to multiple competing polymorphs with distinct crystal symmetries and local structural motifs. Despite these interesting aspects, the experimental exploration and characterization of M_2C compounds have been challenging due to the requirement of high temperature and precise control of processing conditions for their synthesis; thereby leading to difficulties in stabilization and characterization of individual polymorphs [8].

Mapping the complex phase space of M_2C systems and addressing knowledge gap necessitates adaptation of state of the art paradigms such as crystal structure prediction (CSP). Explicit representation of different disorders of M_2C systems in structural models requires consideration of large supercells. This critical requirements forms a major hurdle in application of CSP methods with ab-initio methods such as density functional theory (DFT). But, recent emergence of universal machine learned inter-atomic potentials (MLIPs) and its use with CSP serves as a potential route to bridge the gap. But, they have seldom been used or tested for these specific complex disordered systems [9]. As an representative example of the complexity, all the reported experimental [4, 5] and theoretical [10, 11, 12] phases of Mo_2C comply with the HCP-derived metal frameworks [13]. But, this conventional picture has been recently challenged by our work in Ref. [14] which reports multiple non-HCP derived phases. Further, these systems have potential to host high entropy compounds considering the recent success of MC systems [7].

Within this master's thesis project, we aim to explore the phase space of 2-3 representative M_2C compositions using the Minima-Hopping (MH) CSP method [15, 16], which has the capability to efficiently explore complex chemical systems [17, 18, 19]. The MH runs will be carried out with universal MACE foundation models [20, 21],

to describe the atomic interactions. The primary goal is to understand and map structural diversity across different chemistries. In order to capture different metal-carbon interactions across the transition metal series, representative M_2C compositions will be selected from the $3d$, $4d$, and $5d$ transition-metal chemistries. The generated structures will be filtered, clustered, and analyzed to identify structural motifs and assess their relative thermodynamic stability. This will be subsequently followed by DFT validation primarily through open sourced Quantum-Espresso (QE) package [22]. Where feasible, the resulting DFT dataset will be used to fine-tune the foundation model to improve accuracy of the MLIP and thereby enable more efficient exploration of the selected M_2C compositions.

This work will lead to a better understanding of the diversity of structural motifs across different M_2C chemistries, the role of entropy in phase stabilization and free-energy landscapes, and other thermodynamic properties. In addition, it will provide further insight into the structure-property relationship, particularly with respect to electronic and mechanical properties.

Master's Candidate Profile

Necessary (Required) Skills

- Background in Physics/Chemistry/Material Science with interest in materials modelling
- Good understanding of solid state physics, thermodynamics, crystal structures
- Good programming skills (Python, C++, etc.)
- Good communication skills

Desirable (Optional) Skills

- Experience in conducting first principles calculation and data analysis
- Experience in use of python libraries for computational material science (ASE, Pymatgen, etc.)
- Experience with structure visualization, geometry analysis

References

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