First-principle calculations of high-pressure phase transformations in RuC

JIAN HAO, XIAO TANG, WENJING LI and YINWEI LI(a)

School of Physics and Electronic Engineering, Jiangsu Normal University - Xuzhou 221116, PRC

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Abstract – The structural stabilities of RuC under high pressure have been studied by using first-principle calculations. Results show that RuC transforms from the ZB-type (zinc-blende-type) structure to a tetrahedral structure with space group $I\overline{4}mm$ at $\sim 9.3$ GPa. The $I\overline{4}mm$ structure constructed by RuC$_5$ pyramids is stable up to $\sim 26$ GPa, above which the WC-type structure becomes energetically more favorable. An increase of the coordination number from 4 to 5 and then to 6 is observed accompanied by the phase sequence of ZB type $\rightarrow I\overline{4}mm \rightarrow$ WC type. Band structure calculations reveal that the ZB-type phase is a semiconductor while the $I\overline{4}mm$ and WC-type phases are metallic. Moreover, the mechanical properties of RuC in all three phases are discussed.

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Introduction. – Upon compression, compounds usually undergo several phase transitions due to the alterations in interatomic interactions and the redistribution of the electronic density. Change of the structure can also give rise to dramatic changes in physical properties [1]. If the changes are irreversible, the new phase can be recovered to ambient conditions. Therefore, compression has been an effective way to synthesize new functional materials. A typical example is the man-made diamond, which is a metastable phase at ambient condition after being synthesized at high pressure and high temperature.

In recent years, transition metal carbides (TMCs) have attracted extensive attention due to their remarkable physical properties, such as high stiffness, high hardness, high thermal conductivity and high melting point. Most synthesized TMCs are considered as hard/superhard materials since they show a very high bulk modulus, such as TiC (242 GPa) [2], ZrC (223 GPa) [3], WC (439 GPa) [4] and PtC (303 GPa) [5]. RuC, synthesized about fifty years ago [6,7], was considered as a hard metallic carbide [6]. Basing on the extremely weak X-Ray diffraction data, a hexagonal WC-type structure was roughly postulated for RuC [6]. Recently, by calculating the total energies of selected 10 typical AB-type structures, a cubic ZB-type (zinc-blende-type) structure was proposed to be the ground-state structure of RuC by Tian et al. [8]. Subsequently, Zhao et al. studied the structural stability of RuC under pressure and predicted a phase transition from the ZB type to the WC type at 20 GPa [9]. These works are extremely important since the discovery of these new structures will inevitably advance our understanding of the physical properties of RuC.

In view of our recent first-principle calculations on OsC [10], an orthorhombic $Pmn2_1$ structure was discovered to be stable over the large pressure region of 0–80 GPa. This motivated an investigation of the $Pmn2_1$ structure for RuC, which is a chemical analog of OsC. Here, we have presented a detailed theoretical study on the total energy, electronic and elastic properties of RuC within the ZB-type, WC-type and $Pmn2_1$ structures. Interestingly, we found that the $Pmn2_1$ structure automatically transforms to a tetrahedral $I\overline{4}mm$ structure at all pressures during optimization, which is stable between 9.3 and 26 GPa. A phase sequence of ZB type $\rightarrow I\overline{4}mm \rightarrow$ WC type was thus revealed for RuC under pressure.

Computational methods. – The ab initio structure relaxations were performed using density functional theory (DFT) within the generalized gradient approximation (GGA) [11], as implemented in the Vienna ab initio simulation package (VASP) [12]. The all-electron projector augmented wave (PAW) [13] method was adopted with the
Table 1: Calculated structural parameters of RuC within the ZB-type, WC-type and $I4mm$ structures at selected pressures.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>Lattice parameters ($\text{Å}$)</th>
<th>$V_0$</th>
<th>Atomic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZB type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>$a = 4.602 \ (4.545^{(a)}, \ 4.566^{(b)})$</td>
<td>24.367</td>
<td>Ru 4$a$ (0, 0, 0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C 4$c$ (1/4, 1/4, 1/4)</td>
</tr>
<tr>
<td>$I4mm$</td>
<td></td>
<td>21.818</td>
<td>Ru 2$a$ (0, 0, 0)</td>
</tr>
<tr>
<td>10</td>
<td>$a = 2.854$ \ $c = 5.356$</td>
<td></td>
<td>C 2$a$ (0, 0, 0.628)</td>
</tr>
<tr>
<td>WC type</td>
<td></td>
<td>20.531</td>
<td>Ru 1$a$ (0, 0, 0)</td>
</tr>
<tr>
<td>0</td>
<td>$a = 2.963 \ (2.908^{(c)}, \ 2.921^{(a)})$</td>
<td></td>
<td>C 1$f$ (2/3, 1/3, 1/2)</td>
</tr>
<tr>
<td>30</td>
<td>$a = 2.875$ \ $c = 2.652$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Reference [8].  
(b) Reference [9].  
(c) Reference [6].

plane-wave kinetic energy cutoff of 520 eV. Monkhorst-Pack Brillouin zone sampling grids with the resolution of $2\pi \times 0.03 \text{ Å}^{-1}$ were used, resulting in total energy convergence to better than 1 meV/atom. Elastic constants were calculated by the strain-stress method [14] with grids denser than $2\pi \times 0.02 \text{ Å}^{-1}$. The phonon dispersion curves were computed using the phonopy program [15], which is an open source package of phonon calculations based on the supercell approach [16]. This approach uses the forces obtained by the Hellmann-Feynman theorem calculated from the optimized supercell through the VASP code. We used $3 \times 3 \times 3$ supercells (27 RuC formula units) for all the three phases.

Results and discussion. – After full geometry optimizations, the ZB-type and WC-type structures keep their initial symmetries, as shown in fig. 1. In the ZB-type structure, each Ru (C) atom is bonded with four C (Ru) atoms with Ru-C bond length of 1.98 Å at ambient pressure. For the WC-type structure, each Ru (C) atom is surrounded by six C (Ru) atoms with relative longer Ru-C bond length of 2.179 Å at ambient pressure. In table 1 the structural parameters of the ZB-type and WC-type phases are compared with the available experimental data [6] and earlier theoretical results [8,9]. A good agreement within a 2% interval is found.

The cell parameters and atomic positions for $Pmn_2_1$-RuC were also fully optimized at selected pressures. However, we surprisingly found that the symmetry of $Pmn_2_1$ changes during the optimization. In the $Pmn_2_1$ structure of OsC [10], each Os atom is coordinated by five C atoms, forming distorted OsC$_5$ pyramids. In each OsC$_5$ pyramid, the four bottom Os-C bonds can be classified into two types with slightly different bond lengths, as shown in fig. 1(c). Once the Os is replaced by Ru, the four bottom Ru-C bonds automatically become equal during optimization at all pressures studied. Consequently, standard RuC$_5$ pyramid (Ru-C bond lengths of 1.984 Å and 2.113 Å × 4) is formed and the $Pmn_2_1$ structure transforms to a higher symmetric tetragonal structure with space group $I4mm$ (fig. 1(d)).

Figure 2(a) presents the calculated enthalpies of the ZB-type and WC-type structures with respect to the $I4mm$ structure. One observes obviously that the $I4mm$ structure becomes energetically more favorable than the ZB type above 9.3 GPa. The $I4mm$ structure is stable up to 26 GPa, above which the WC-type structure takes over. According to our enthalpy results, a phase sequence of ZB type $\rightarrow$ $I4mm$ $\rightarrow$ WC type was thus uncovered for RuC.
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Fig. 2: (Color online) (a) Enthalpies of the earlier proposed ZB-type and WC-type structures relative to our predicted I4mm structure as a function of pressure. (b)–(d) show the calculated phonon dispersions of RuC with the ZB-type, I4mm and WC-type structures at ambient pressure. Dashed red lines in (d) represent the phonon dispersions of the WC-type structure at 30 GPa.

Fig. 3: (Color online) The calculated volume incompressibility (V/V₀) of RuC and diamond. Insets show the incompressibility along the a-axis (a/a₀) and the c-axis (c/c₀).

with an increase of coordination number from 4 to 5 and then to 6.

To check the structural stabilities of the three phases of RuC, the phonon dispersions and elastic constants were calculated, as shown in fig. 2 and table 2. The phonon dispersions of the ZB-type and I4mm structures at high pressures are not shown since no imaginary frequency was found. Results show that the ZB-type and I4mm structures are both dynamically and mechanically stable at all pressures studied while the WC-type structure is only stable within its pressure stability field. This results suggest that the newly predicted I4mm phase can be recovered to ambient conditions once synthesized at high pressure, suitable for potential applications.
Fig. 4: (Color online) (a) Calculated band structures and partial density of states (DOS in unit of states/eV/f.u.) of RuC with the ZB-type (a), I4mm (b) and WC-type (c) structures. Horizontal lines at zero energy are the Fermi levels.

Fig. 5: (Color online) The total charge density contours of RuC with the ZB-type (a), I4mm (b) and WC-type (c) structures.

Table 2: The calculated elastic constants $C_{ij}$ (GPa), bulk modulus $B$ (GPa) and shear modulus $G$ (GPa) and $B/G$ ratio of RuC with the ZB-type, I4mm and WC-type structures.

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$B$</th>
<th>$G$</th>
<th>$B/G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZB type</td>
<td>330</td>
<td>81</td>
<td>198</td>
<td>242</td>
<td>74</td>
<td>3.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I4mm</td>
<td>516</td>
<td>427</td>
<td>63</td>
<td>75</td>
<td>212</td>
<td>182</td>
<td>286</td>
<td>85</td>
<td>3.36</td>
</tr>
<tr>
<td>WC type</td>
<td>396</td>
<td>700</td>
<td>76</td>
<td>307</td>
<td>199</td>
<td>316</td>
<td>66</td>
<td>4.79</td>
<td></td>
</tr>
</tbody>
</table>

The mechanical properties of RuC, such as incompressibility, elastic constant, and brittleness are important for potential technological and industrial applications. To compare the incompressibility of the three phases of RuC, the incompressibility of volume and along the a-axis and c-axis as a function of pressure has been plotted in fig. 3. It is found that the order of incompressibility for RuC is WC type $> I4mm >$ ZB type, as can also be deduced from their bulk moduli listed in table 2, 316 GPa for the WC-type phase, 286 GPa for the I4mm phase and 242 GPa for the ZB-type phase. It is also found that the 14mm and WC-type phases possess the highest incompressibility along the a-axis and c-axis, respectively (fig. 3), in accordance with the calculated largest $C_{11}$ in I4mm and $C_{33}$ in WC type. Surprisingly, we found that the incompressibility of RuC is only slightly lower than that of diamond (fig. 3), indicating that RuC is an ultra-incompressible material. Moreover, we observed very high values of $B/G$ (bulk/shear modulus ratio) for RuC in all three phases. It has shown that a high or low $B/G$ value is often associated with ductility or brittleness, and the critical value that separates ductility and brittleness is $\sim 1.75$ [17]. We, therefore, concluded that RuC is a ductile material.

It is interesting to examine the relationship between the electronic properties and mechanical properties (e.g., bulk modulus). Our band structure calculations (fig. 4) show that, contrary to the semiconductivity of the ZB-type phase, both I4mm and WC-type phases are metallic with several dispersion bands crossing the Fermi level ($E_F$). The partial densities of states (DOS) of three phases of RuC were also studied to make sense of the bonding properties. From fig. 4, it can be seen that there is a strong hybridization between the Ru-$d$ and C-$p$ states near the Fermi level in all three phases. It is the strong hybridization that indicates the covalent bonding and leads to a separation of the bonding states. Moreover, the charge density distributions (fig. 5) clearly reveal strong directional covalent Ru-C bonds in three phases, which may explain the high bulk modulus of RuC.
Conclusions. – In summary, in addition to the previous proposed ZB-type and WC-type structures, we have found a novel structure for RuC with space group \( I4_{1}mm \), which is thermodynamically stable in the pressure range of 9.3–26 GPa. A phase diagram of ZB type \( \rightarrow I4_{1}mm \rightarrow WC \) type was thus revealed for RuC. The transition follows the elevated 4, 5 and 6 coordination numbers. Intuitively, this might be as expected under pressure but reveals rich bonding capability of heavy transition metals. Results also indicate that RuC with three phases possess excellent mechanical properties, which are important for potential technological and industrial applications.

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