A high-pressure study of Cr_3C_2 by XRD and DFT*

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(Received 14 February 2020; revised manuscript received 6 April 2020; accepted manuscript online 23 April 2020)

The equation of state (EOS) of Cr_3C_2 at high pressure is studied by the synchrotron radiation x-ray diffraction (XRD) in a diamond anvil cell (DAC) at ambient temperature, and density functional theory (DFT). The XRD analysis shows that the orthorhombic structure is maintained to a maximum pressure of 44.5 GPa. The XRD data show that the bulk modulus is $K_0 = 292(18)$ GPa with $K_0' = 3.25(0.85)$. In addition, the high-pressure compression behavior of Cr_3C_2 is studied by first principles calculations. The obtained bulk modulus of Cr_3C_2 is 323 (1) GPa.

Keywords: equation of state, Cr_3C_2, high pressure, *in-situ* XRD, first principles calculations

PACS: 64.30.Jk, 64.60.–i, 07.35.+k, 61.05.cp **DOI:** 10.1088/1674-1056/ab8c3d

1. Introduction

Crystal Cr_3C_2 is a kind of high melting point material with good wear resistance, corrosion resistance, and oxidation resistance in high temperature environment. It can be widely used in aircraft engines and petrochemical mechanical devices, and can greatly improve the service life of machinery.[1–3] So far, Cr_3C_2 has aroused the great interest of researchers.[4–10] Kuriyama *et al*. investigated the electrical conductivity of the Cr_3C_2 at different sintering temperatures.[4] Ma *et al.* obtained the Cr_3C_2 with a hardness $H_v = 18$ GPa.[5] Hirota *et al.* derived a hardness of $H_v = 18.9$ GPa for Cr_3C_2.[6] Min *et al.* calculated the structure, electronic properties, *etc*. of Cr_3C_2 by using density functional theory.[7] Li *et al.* calculated a hardness of 20.9 GPa of Cr_3C_2 by using the first principles calculations.[8] Jiang investigated the structure, elastic and electronic properties of Cr_3C_2 by using first principles calculations.[9] Jiang *et al.* obtained a hardness of 20.3 GPa for Cr_3C_2.[10]

Pressure can reduce the atomic distance, change the electronic shell state and crystal cell structure, and then change its structure, physical and chemical properties, such as high-pressure structural phase transition, high-pressure strength, high-pressure texture.[11] High pressure science is an interdisciplinary science, which has been integrated with physics, material science, geoscience, chemistry, and other disciplines, and thus greatly promoting its application and development and its relevant fields as well, and it is an important field of basic research and applied science research. The physical and chemical properties of Cr_3C_2 under high pressure are closely related to its crystal composition. Therefore, a thorough understanding of the crystal composition of Cr_3C_2 is helpful in improving the scientific use of Cr_3C_2.

Although the Cr_3C_2 has been studied,[4–10] there is no direct experimental measurement nor theoretical calculation for its high-pressure EOS. Therefore, the equations of state (EOSs) of Cr_3C_2 under the pressures up to 44.5 GPa is studied in a diamond anvil cell (DAC) with silicon oil as pressure medium by using angle dispersive XRD technology, and the EOSs of Cr_3C_2 under pressures up to 50 GPa were calculated based on DFT in this study.

2. Experimental details

The Cr_3C_2 (99.5%) samples was purchased from a company. Under ambient conditions, Cr_3C_2 has an orthorhombic structure (the space group is *Pnam*, as shown in Fig. 1). We used the scanning electron microscope (SEM) to analyze the the sample of Cr_3C_2. The SEM test of Cr_3C_2 was completed in the Analytical and Testing Center of Sichuan University, China. The model of SEM instrument is JSM-7500 F, resolution is 1.0 nm (15 kV), and magnification is 25–8 $\times 10^5$. The SEM image shows that the average cluster size of the black polycrystalline powders is 3 μm (see Fig. 2), and the grain size of Cr_3C_2 is homogeneous. The x-ray diffraction experiment of copper target was completed in the Analytical and Testing Center of Sichuan University. The model of XRD instrument is EMPYREAN, 2θ angle is in a range from -110° to 162°, the minimum controllable step is 0.0001°, resolution is FWHM $= 0.028^\circ$, and wavelength is $\lambda = 1.5406$ Å. Figure 3

*Project supported by the Project of Ph. D. Special Research of Sichuan University of Arts and Science, China (Grant No. 2019BS006Z) and the Fund from the Chinese Academy of Sciences (Grant Nos. KJCX2-SW-N03 and KJCX2-SW-N20).

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shows the representative XRD patterns of Cr_3C_2 powder under ambient conditions, and the derived lattice parameters are $a =$ 5.532(0.001) Å, $b = 11.500(0.002)$ Å, $c = 2.8318(0.0003)$ Å, respectively. In the high-pressure XRD experiment, a modified Mao bell DAC with a diameter of 300 μm was used. We pre-indented a T301 gasket to ∼ 35 μm, and made sample hole with a diameter of 120 μm by laser. We used silicone oil as a pressure medium. A ruby chip with a diameter of 10 μm was placed on the top of the sample center, and used as a pressure sensor.[12]

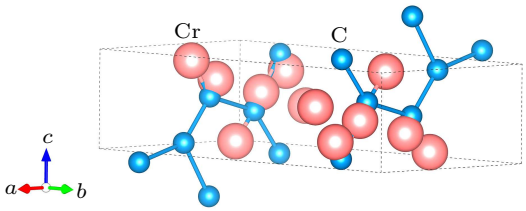

Fig. 1. Crystal structure of Cr_3C_2 in ambient condition.

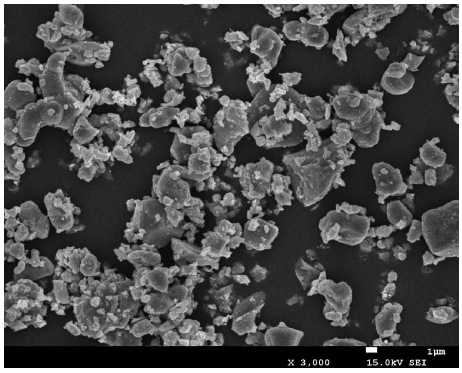

Fig. 2. SEM image of Cr_3C_2 sample in ambient conditions.

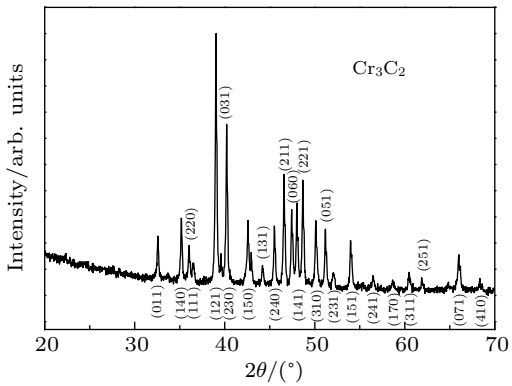

Fig. 3. Representative powder XRD of Cr_3C_2 in ambient conditions with each peak marked by corresponding Miller indices, and x-ray wavelength $\lambda = 1.5406$ Å.

The high-pressure XRD experiments of *in-situ* synchrotron radiation were carried out on 4w2 beam line of Beijing Synchrotron Radiation Facility (BSRF). PILATUS detector was used to receive the diffraction pattern, and CeO_2 standard was used to calibrate the distance between the sample and the detector and the orientation of the detector. Each XRD pattern was obtained from the sample that has been exposed to the beam for 5 min–8 min. We used fit2d software[13] to process and analyze the XRD patterns.

3. Theoretical calculation details

The DFT calculations were carried out by using the Vienna *ab-initio* simulation package (VASP).[14] In addition, DFT calculations include structural optimization and enthalpy, in which the Perdew–Burke–Ernzerho[15] was applied to exchange–correlation functions. The interaction between the real electron and the valence electron of the ion was calculated by the projection affixed plane wave (PAW) method. The valence electrons of C and Cr were $2s^22p^2$ and $3d^54s^1$, respectively. Monkhorst pack method was applied to the Brillouin region integration of Cr_3C_2 system, and the integration grid was $8\times8\times8$. The truncation energy of plane wave basis function was measured, and its convergence accuracy was less than 2×10^{-3} eV, and the value of 600 eV was given. Cr_3C_2 had an orthorhombic structure (space group *Pnam*) with lattice parameters $a = 5.4767$ Å, $b = 11.4621$ Å, $c = 2.7882$ Å, and $\alpha = \beta = \gamma = 90°$ in ambient conditions. Using the third-order Birch–Murnaghan equation to fit the volume–pressure data, the bulk modulus (K_0) and its first derivative (K_0') are obtained.

4. Results and discussion

The diffraction patterns obtained are analyzed with fit2d software.[13] The maximum pressure of the experiment is 44.5 GPa, and the pressure value is given by ruby sensor.[12] The diffraction patterns of Cr_3C_2 at different pressures are shown in Fig. 4. Several peaks of (011), (101), (121), (230), (151) can be seen in the whole pressure range. The orthorhombic structure is maintained to a maximum pressure of 44.5 GPa.

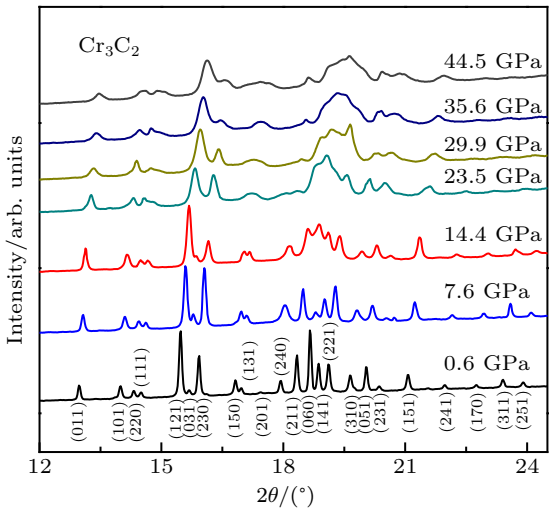

Fig. 4. Representative XRD patterns of Cr_3C_2 under different pressures.

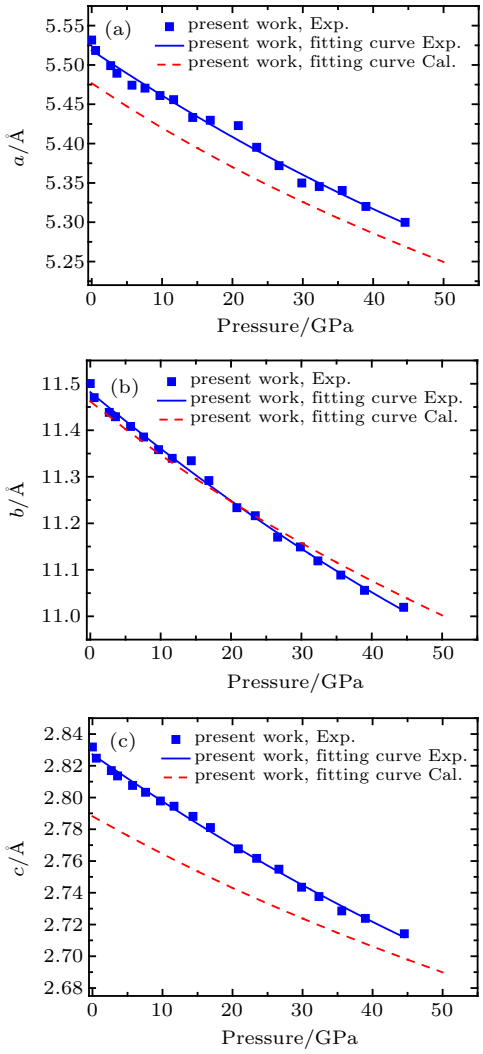

Fig. 5. Compressibility of lattice parameters of Cr_3C_2 and calculation result in generalized-gradient approximation (GGA).

The lattice parameters and the equivalent unit cell volume of Cr_3C_2 under different pressures are fitted by d-spacings of $d(011)$, $d(101)$, $d(121)$, $d(230)$, $d(151)$. The compressibility of a/a_0, b/b_0, and c/c_0 in the orthorhombic structure of Cr_3C_2 is shown in Fig. 5, respectively. The a, b, and c axes of the orthorhombic system decrease with pressure increasing.

The unit cell volume of the compression curve of experimental result and GGA calculation result are shown in Fig. 6. The results show that the orthorhombic structure of Cr_3C_2 is stable to the highest pressure of 44.5 GPa, and there is no phase transition.

The third-order Birch–Murnaghan equation is used to fit the change of cell volume with pressure. And we can obtain the K_0 and K_0' in this way. The third-order Birch–Murnaghan equation is expressed as[16]

$$P = 1.5K_0\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right] \times\left\{1+\frac{3}{4}(K_0'-4)\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]\right\}, \quad (1)$$

where K_0 and K_0' are the bulk modulus and its derivative with respective to pressure in ambient conditions, respectively, and V_0 is the volume in ambient conditions.

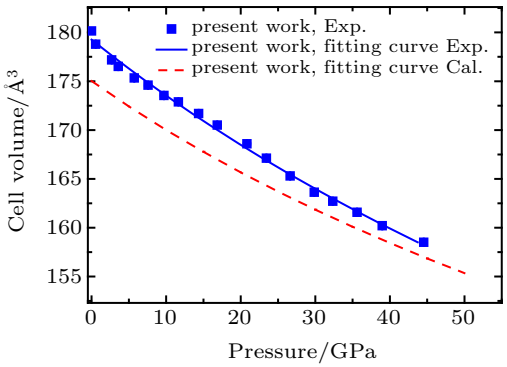

Fig. 6. Compression curve of Cr_3C_2 derived from lattice parameters, with Birch–Murnaghan fitting line based on experimental data (blue) and Birch–Murnaghan equation fitting to theoretical calculation result (red dotted).

The bulk modulus and its first derivative with respective to pressure of the orthorhombic structure are 292(18) GPa and 3.25(0.85), respectively. The theoretical calculation result is 323(1) GPa. It can be seen that the experimental bulk modulus in present work is 10% lower than the GGA calculation result in present work. As the DFT transforms the real multi-electron problem into a single-electron problem to calculate single-electron effective potential, the total energy of electron gas is only a function of electron density, and the corresponding density is the ground state density of a single particle. The exchange correlation energy in the GGA approximation is related to density and the density gradient. In addition, the temperature of electrons in a real material in ambient conditions is not absolute zero compared with in the GGA approximation. Thus, the bulk modulus of Cr_3C_2 needs further studying. The values of bulk modulus (K_0), its derivative with respect to pressure (K_0') of carbides obtained by various methods are shown in Table 1. It can be seen that the elastic modulus of Cr_3C_2 is higher than that for each of TiC, ZrC, and HfC.

We calculate the electronic structure of Cr_3C_2 at high pressure. Figure 7 shows the electron band structure of Cr_3C_2 in the selected highly symmetric direction, where the Fermi level is set to be zero. It can be seen from the band structure that Cr_3C_2 is a semimetallic compound, as its electron orbit occupies the Fermi energy level. In addition, the electronic structure of Cr_3C_2 has no change with the increase of pressure. With the aid of the electronic density of state (DOS), the structure of Cr_3C_2 can be well understood (Fig. 8). It can be seen that the DOSs in the spin-up precess and the DOSs in spin-down process with pressure increasing from ambient pressure to 30 GPa are indentical as fhown in Fig. 8, indicating that Cr_3C_2 is not magnetic in the whole pressure range.

Table 1. Values of bulk modulus (K_0) and its derivative with respect to pressure (K_0') of carbides obtained with various methods.

Solids	Methods	K_0/GPa	K_0'
Cr_3C_2	present-Exp.	292(18)	3.25(0.85)
	present-Cal.	323(1)^{GGA}	
TiC	Exp.	233,[17] 263,[18] 240[19]	–
	Cal.	252.80,[20] 273,[21] 251,[22] 257,[18] 228,[23] 270[24]	4.05[20]
ZrC	Exp.	234,[18] 223,[25,26] 230,[27] 207,[28] 220[29]	–
	Cal.	222.88,[20] 237,[21] 217,[30] 224.3,[31] 217.7[32] 232,[33] 224,[34] 225,[35] 230.5,[36] 229,[37] 265[23] 217.7,[32] 220.1,[38] 222,[39]	4.05,[20] 3.86[34]
HfC	Exp.	–	–
	Cal.	310.33,[20] 228.2,[40] 236,[30] 218,[23] 265[41]	2.908,[20] 3.88[40]

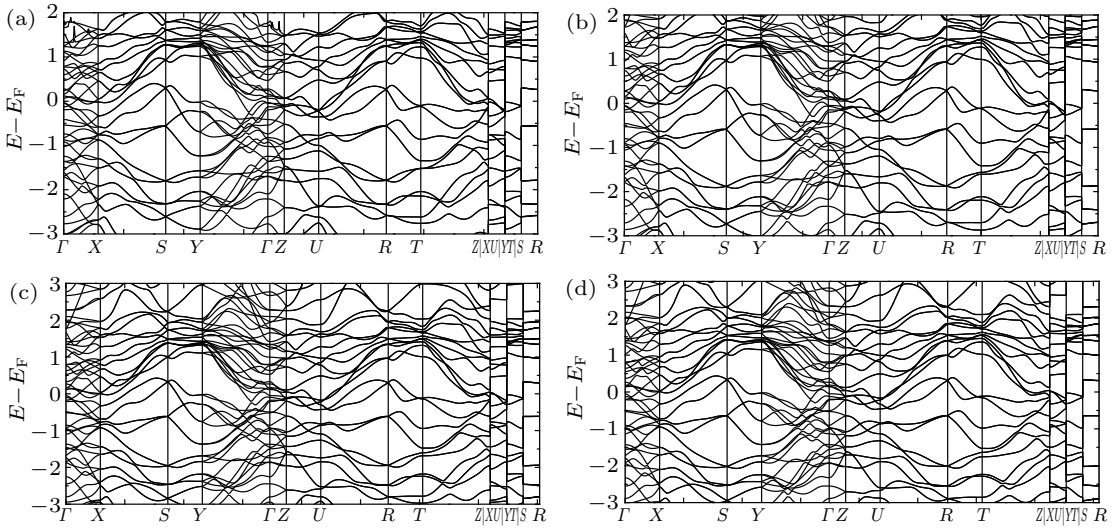

Fig. 7. Calculated band structure of Cr_3C_2 at (a) 0 GPa, (b) 10 GPa, (c) 20 GPa, and (d) 30 GPa.

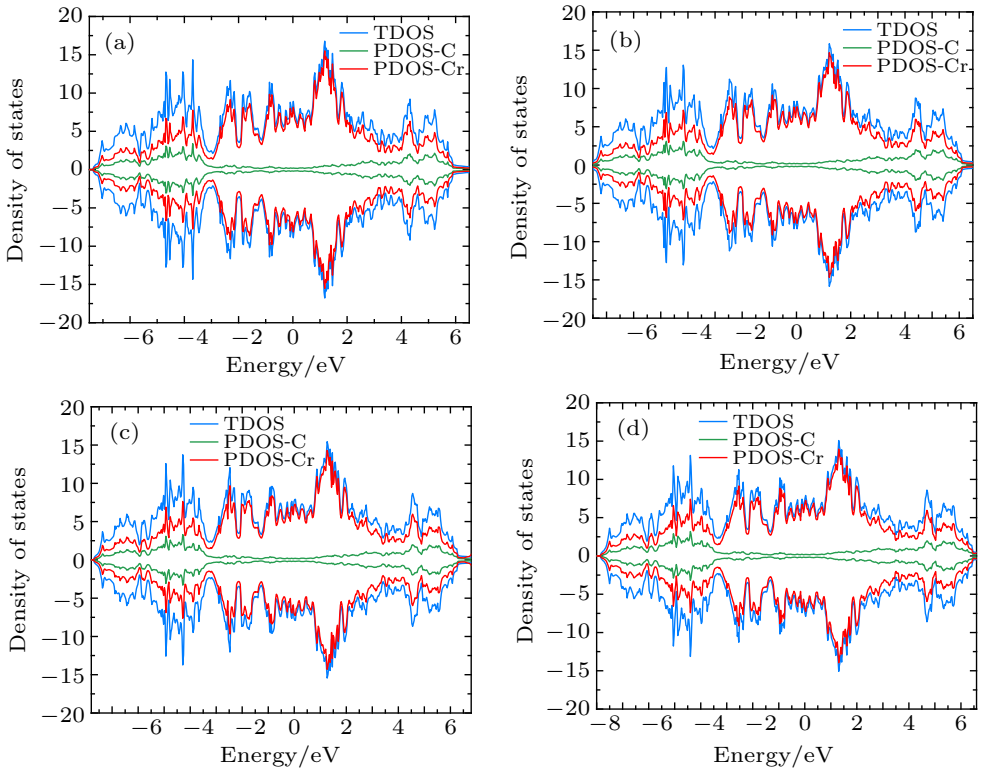

Fig. 8. Calculated total DOS and PDOS of Cr_3C_2 at (a) 0 GPa, (b) 10 GPa, (c) 20 GPa, and (d) 30 GPa.

5. Conclusions

In this work, we studied the EOSs of Cr_3C_2 in the modified Mao–Bell DAC under quasi-static compression at pressures up to 44.5 GPa by XRD at room temperature. The orthorhombic structure of Cr_3C_2 is stable at pressures up to the highest pressure of 44.5 GPa without phase transition. The bulk modulus of XRD is 292(18) GPa and its first derivative with respect to pressure is 3.25(0.85). The calculated bulk modulus is 323(1) GPa. The results show that the bulk modulus calculated in the GGA is slightly higher than the experimental results.

Acknowledgement

The experiment in this work was performed at 4W2 beamline of Beijing Synchrotron Radiation Facility (BSRF).

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