

## High-Pressure and Electronic Band Structure Studies on Mo<sub>2</sub>BC

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**Abstract** In this work, high-pressure electrical resistivity measurements and electronic structure analysis on the intermetallic Mo<sub>2</sub>BC system are presented. Electrical resistivity measurements up to about 5 GPa using a diamond anvil cell on Mo<sub>2</sub>BC revealed that  $T_c$  decreases in a non-monotonic way. Using Linearized Augmented Plane Wave method based on Density Functional Theory, we investigate the changes in the electronic structure of this compound as a function of pressure. The states at the Fermi level mainly come from the  $d$  orbitals of molybdenum atoms. As the pressure increases, the band width is enhanced and the total density of states at the Fermi level decreases. The Fermi surface for this compound possesses a two-dimensional character which prevails under an applied pressure of about 10 GPa. The results are compared with the chemical pressure effects on  $T_c$  induced by the gradual and non-simultaneous elimination of B and C in the compound.

**Keywords** Superconductivity · High pressure · Electronic bands · Fermi surface

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## 1 Introduction

Superconductors containing light elements, such as boron and/or carbon, have attracted noticeable interest at the last 2 decades due to their singular electronic and structural properties. Two examples are the borocarbides  $RT_2B_2C$  ( $R = Y, Lu$ , rare earths, and  $T =$  transition elements) [1, 2] and the compound  $MgB_2$  [3]. The first one being a new class of intermetallic superconductors that allowed to study the interplay between magnetism and superconductivity at relatively high  $T_c$ , ( $T_c = 23\text{ K}$  in  $YPd_2B_2C$ ), and the second one, the binary system with the highest  $T_c$  (at about 40 K) of the binary superconductors. Boron has the tendency to form zigzag chains, nets, and three-dimensional networks [4] which combined with the availability of C for bonding could conform structures with interesting mechanical and electronic properties. Such is the case for the Mo-based compounds ( $Mo_2B$ ,  $Mo_2C$ ,  $Mo_2BC$ ), some of them with refractory [5], unusual stiffness and hardness [6–8], catalyst [9, 10], and superconducting [11, 12] characteristics. From the electronic point of view, dimolybdenum boride  $Mo_2B$  (body-centered tetragonal unit cell, space group:  $I4/mcm$ ) and dimolybdenum carbide  $Mo_2C$  (face-centered orthorhombic unit cell, space group  $Pbcn$ ) are both superconductors with  $T_c$  at 5.8 [13] and 7.3 K [14], respectively. On the other hand,  $Mo_2BC$  possesses a face-centered orthorhombic symmetry (space group:  $Cmcm$ ) and is a superconductor with  $T_c$  ranging from 6.3 to 7.5 K [15, 16]. Accordingly, the non-simultaneous extraction of C and B from  $Mo_2BC$  decreases  $T_c$ , but it is more pronounced for the C case.

In  $Mo_2BC$ , it is known that the Mo substitution by other transition elements, such as Ti, V, Cr, Nb, Ta, and W, does not form the  $Mo_2BC$ -type structure [17]; however, Zr, Nb, Rh, Hf, Ta, and W have been substituted to a significant extent ( $x = 0.15–1.10$ ) in  $Mo_{2-x}M_xBC$  [16, 18] and, with exception for Rh-containing alloy,  $T_c$  significantly decreases with increasing  $x$  for all the alloys. Interestingly, for the case of Rh,  $T_c$  at first increases up to 9 K and then decreases for  $x$  ranging from 0 to 0.39. Comparing the atomic radii (calculated and covalent) for the last atoms, it is noted that Rh possesses the smallest one of all them, which suggests that some critical chemical pressure tunes up the observed superconducting changes. However, the decrease of  $T_c$  under the negative chemical pressure (the cell volume increases) generated by the substitution of relatively bigger (Hf, Zr, Ta, Nb, W) atoms than Mo is not so clear, which could be due to electronic and/or phononic changes. This work focuses on the study of the effect of the applied external pressure on the superconducting properties of the  $Mo_2BC$  system. In order to explain the observed changes in the electronic properties, the electronic structure of this compound for different pressure values was also calculated.

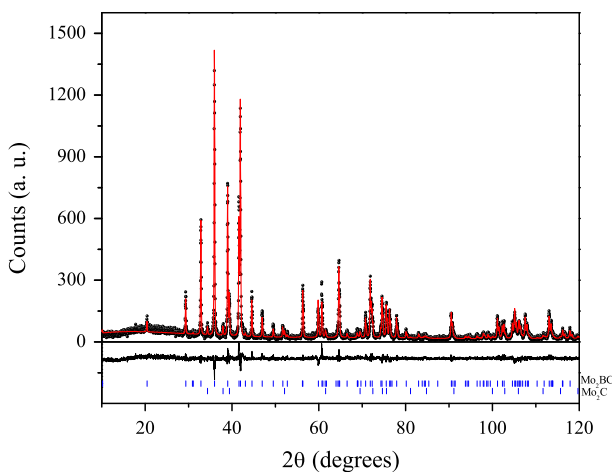
## 2 Experimental and Computational Details

Polycrystalline samples of  $Mo_2BC$  were obtained by melting stoichiometric amounts of high-purity molybdenum powder (99.9 % Aldrich), boron pieces (99.99 % Aldrich), and carbon graphite rod (99.995 % Aldrich) under flowing ultra-high-purity argon gas in an arc melting furnace. Samples were re-melted several times and after a temperature-controlled annealing treatment at about 800 °C and 24 h, they were char-

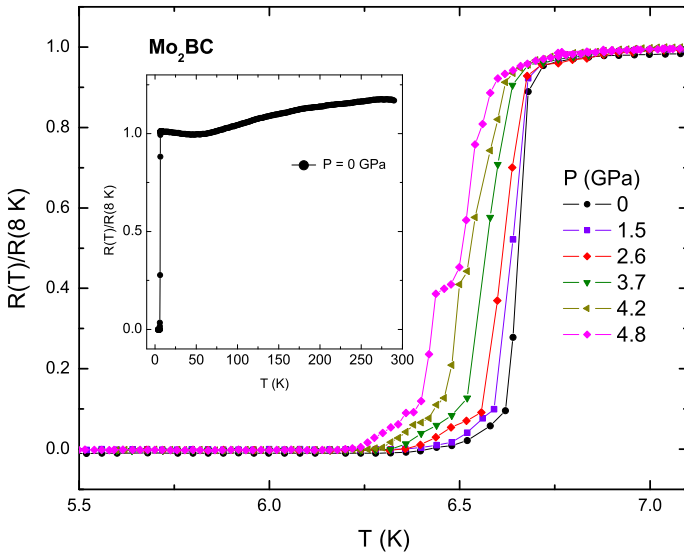
acterized by X-ray diffraction technique. Phase identification was performed with an X-ray diffractometer (XRD) Siemens D5000 using Cu  $K\alpha$  radiation and an Ni filter. Intensities were measured in steps of  $0.02^\circ\text{C}$  from  $5$  to  $120^\circ\text{C}$  at room temperature. Refinement of the crystal structure was performed with the program Fullprof [19]. Resistivity measurements as a function of temperature and pressure were performed using a four-probe method. The quasi-hydrostatic pressure was provided by a micro cryogenic diamond anvil cell (MCDAC) using MgO powder as a transmitting pressure medium. In order to measure the pressure in situ, a Pb manometer close to the sample was used [20]. The experiments were performed from room temperature to  $4\text{ K}$ . Quantum mechanical calculations were done with the WIEN2k package [21], which is a linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT). The generalized gradient approximation of Perdew, Burke, and Ernzerhof [22] was used for the treatment of the exchange–correlation interactions. The calculation was relativistic to take into account relativistic effects in Mo atoms [23]. The energy threshold to separate localized and non-localized electronic states was  $-6\text{ Ry}$ . The muffin-tin radii were:  $2.07 a_0$  for molybdenum,  $1.68 a_0$  for boron, and  $1.84 a_0$  for carbon ( $a_0$  is the Bohr radius). The criterion for the number of plane waves was  $K_{\text{MT}}^{\text{min}} \times K^{\text{max}} = 9$ , and the number of  $k$ -points were 462 ( $7 \times 11 \times 6$ ). To find the effect of pressure, the muffin-tin radii were reduced  $6\%$ , the volume was varied from  $-15$  to  $+3\%$  in steps of  $3\%$ , and the energy was adjusted to a Birch–Murnaham equation. For crystal structure visualization, the XCrySDen package [24] was used.

### 3 Results and Discussion

Figure 1 shows the powder X-ray diffraction pattern of the polycrystalline  $\text{Mo}_2\text{BC}$  sample. All the intensity peaks were analyzed and showed that the majority phase corresponds to  $\text{Mo}_2\text{BC}$ . Also a minority phase corresponding to the orthorhombic  $\text{Mo}_2\text{C}$



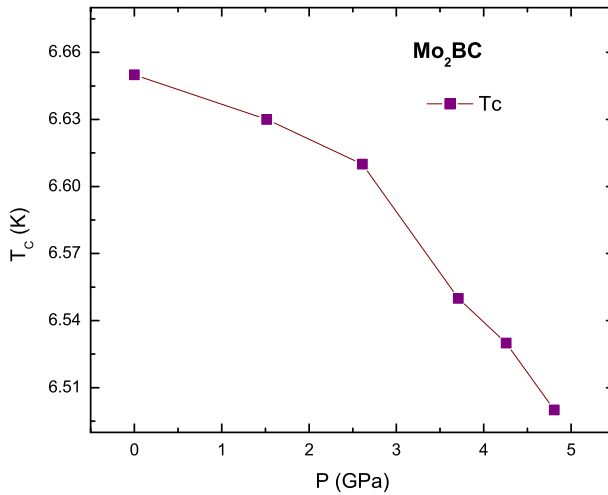
**Fig. 1** Diffraction pattern of the polycrystalline  $\text{Mo}_2\text{BC}$  sample and Rietveld refinements. Minor phase detected corresponds to  $\text{Mo}_2\text{C}$  (Color figure online)



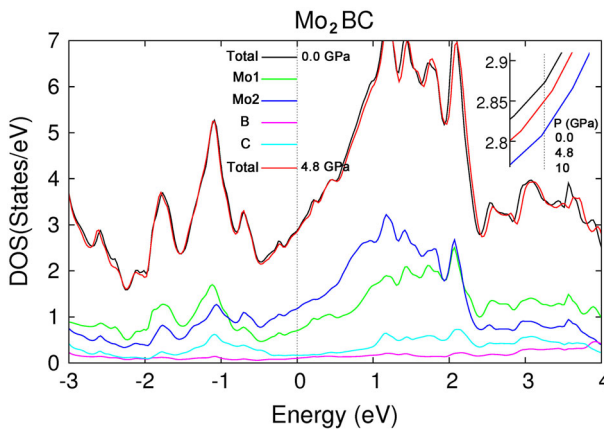
**Fig. 2** Normalized electrical resistance as a function of temperature and pressure for Mo<sub>2</sub>BC. *Inset* shows the  $R(T)/R(8\text{ K})$  behavior at room pressure (Color figure online)

system was observed. The obtained cell parameters using X-ray Rietveld refinements for Mo<sub>2</sub>BC were  $a = 3.1042(2)\text{Å}$ ,  $b = 17.5022(1)\text{Å}$ , and  $c = 3.0611(2)\text{Å}$  in good agreement with the reported values [25,26]. From the refinement, the Mo–Mo atomic distance in the Mo<sub>2</sub>BC structure is bigger than that in the Mo metal (with a BCC structure, the stable phase at room pressure). This effect can be explained due to the presence of C and B chains in the Mo<sub>2</sub>BC structure. Figure 2 shows a plot of the normalized electrical resistance as a function of temperature and pressure for Mo<sub>2</sub>BC. At room pressure, the compound behaves metallic with the electrical resistance decreasing monotonically down to about 55 K. Lowering the temperature, the R–T curve reveals a flat minimum at about 50 K (see inset of Fig. 2), and later it becomes superconducting at 6.65 K with a transition temperature width of 0.36 K ( $T_c$  was defined as the transition midpoint). This  $T_c$  value is in accord with that reported in the literature [15]. In order to get more insight into the superconducting behavior of Mo<sub>2</sub>BC, the system was subjected to different external applied pressures of up to about 4.8 GPa, and as it can be clearly seen in Fig. 2, the superconducting transition temperature decreases as the pressure increases.

Figure 3 shows the corresponding  $T_c$  versus  $P$  curve. The applied pressure of up to 4.8 GPa induces a non-linear decreasing of  $T_c$ . For the plot, it is possible to distinguish two linear regions; for pressures lower than 2.6 GPa,  $T_c$  decreases at a rate of  $-0.015\text{ K/GPa}$ . Between 2.6 and 4.8 GPa,  $T_c$  decreases faster at a rate of  $-0.04\text{ K/GPa}$ . Such a negative rate is comparable to that of conventional metallic superconductors and commonly seen in transition metals. Interestingly, a negative  $dT_c/dP$  rate has been observed in several other compounds having the light element B [27–29]. The feature like a bump observed in the normalized resistivity for 3.7 and 4.8 GPa at low temperature could be related to the presence of the superconducting Mo<sub>2</sub>C (small



**Fig. 3** The variation of the superconducting transition temperature as a function of pressure for Mo<sub>2</sub>BC. Lines are guides to the eye (Color figure online)



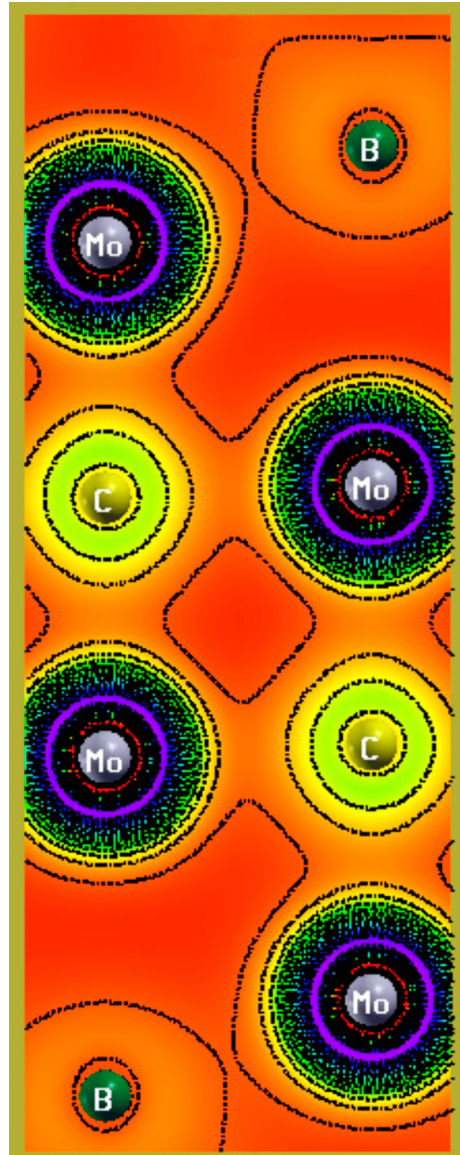
**Fig. 4** Calculated density of states for Mo<sub>2</sub>BC at selected pressures. The main contribution at  $E_F$  is from the transition element. B and C have small contributions. DOS at  $E_F$  decreases with pressure. Inset: Zoom of DOS at  $E_F$  for 0, 4.8, and 10 GPa (Color figure online)

traces, according to the XRD). It is important to point out that the same behavior was also observed in another Mo<sub>2</sub>BC sample.

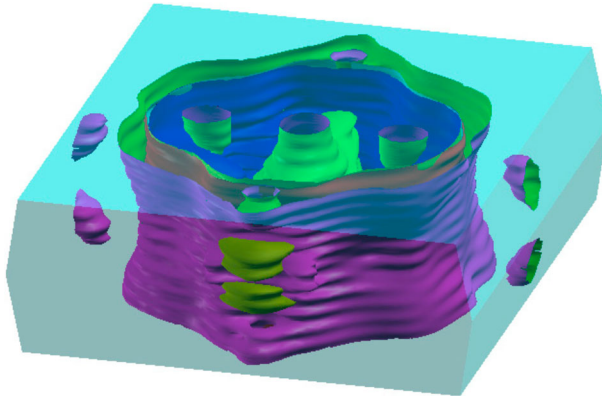
The small decreasing of  $T_c$  observed under external pressure applied can be contrasted with its decrement induced by a positive chemical pressure (compression) as resulting from the non-simultaneous elimination of B and C in Mo<sub>2</sub>BC. Considering the similar radii of B and C, this  $T_c$  reduction by chemical pressure effect can be routed to some change in the electronic structure of the compound due to the shrinking of the unit cell.

The electronic bands, electronic density of states (DOS), and charge density of Mo<sub>2</sub>BC at different pressures were calculated using ab initio calculations based on density functional theory. Figure 4 shows the DOS at two selected pressures, 0 and 4.8

**Fig. 5** Electronic charge density in the (110) plane for  $\text{Mo}_2\text{BC}$  at ambient pressure (Color figure online)



GPa, which indicates the metallic character of the compound. At ambient pressure, the DOS at the Fermi energy is 2.81 states/eV and it stems primarily from Mo 4*d* states, while the contributions of B 2*s* and 2*p*, and C 2*s* and 2*p* states are almost negligible. The Fermi energy  $E_F$  is located near to a local minimum of the DOS. The DOS interstitial contribution was also calculated and its value was considerably large, as it corresponds to metallic systems, and of the same order than that for Mo atom. DOS at the Fermi level for  $\text{Mo}_2\text{BC}$  subjected at several pressures from 0 up to about 10 GPa was determined (inset of Fig. 4). Under such high pressure value, DOS decreases 2.8



**Fig. 6** Topology of the Fermi surfaces at room pressure for  $\text{Mo}_2\text{BC}$  (Color figure online)

% and the bands widen (not shown). This is a result of a larger atomic overlap and the electrical conductivity increases. For 10 GPa, the volume reduction corresponds to 2.5 %, and for 4.8 GPa corresponds to 1.2 % (0.4 % for the cell parameters). For the  $-15$  % volume, the cell parameters,  $a$ ,  $b$ , and  $c$ , were optimized, but the relative values did not change significantly; for a metallic compound, such as the present one, this is the normal result. On the other hand, the calculated density of charge in several structural planes revealed that, at ambient pressure, the isolines surround the atoms and in the interstitial region have low but constant electron density; these two points are indicative of a metallic bond. Figure 5 shows mapping of the contour lines particularly for the projected charge density on the (110) plane at room pressure. Accordingly, traces of covalent bond between Mo and C and of ionic character between Mo and B are found. Fermi surfaces at room pressure were also calculated (see Fig. 6), and a tubular character was revealed which is an indicative of the two-dimensional (2D) character of the electric conduction. Under a pressure of about 10 GPa, calculations show that such a dimensional character prevails unaltered. The observed widening of the bands with pressure and the corresponding lowering of DOS at  $E_F$  imply a higher electron velocity which could affect the electron–phonon coupling. Considering the high bulk modulus of  $\text{Mo}_2\text{BC}$  ( $\sim 313$  GPa [7]), at first approximation the small negative value of  $dT_c/dP$  in this compound, in the range of pressure studied here, can be related to the small decrease in the electronic DOS  $N(E_F)$ . On the other hand, the fact that the elimination of C from  $\text{Mo}_2\text{BC}$  compresses the cell and decreases  $T_c$  and, separately, that the substitution of Mo by bigger but not necessarily more heavy atoms (Hf, Zr, Ta, Nb, W) also decreases  $T_c$  suggests that such chemical pressure affects  $T_c$  mainly by changes in electronic nature. Further studies are now being made in order to elucidate if external pressure significantly changes the vibrational frequencies and also to calculate the  $T_c(P)$  equation of state [30].

#### 4 Summary

In this work, we performed electrical resistivity measurements under pressures of up to about 5 GPa and ab initio calculations of the electronic bands for  $\text{Mo}_2\text{BC}$  at several

pressures. The applied pressure of up to 4.8 GPa induces a non-linear reduction of  $T_c$  which is larger for pressures above 2.6 GPa and at least up to about 5 GPa. Results of the calculated DOS indicate that its value is slightly decreased under pressure. Possibly, the origin of the  $T_c$  reduction by external pressure can be of electronic nature. This  $T_c$  behavior under pressure is similar to what already was observed in several other superconducting compounds having the light element B. It is important also to mention that the Fermi surface is highly anisotropic with a 2D character, remaining almost unchanged under a pressure of about 10 GPa.

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