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# Experimental and theoretical investigation of Mo<sub>2</sub>C at high pressure

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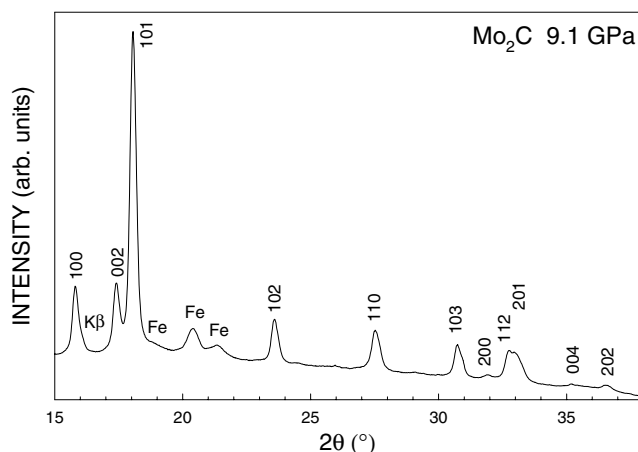
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## Abstract

Molybdenum hemicarbide was investigated by angle-dispersive, x-ray diffraction in a diamond anvil cell at high pressure and by theoretical methods. Mo<sub>2</sub>C is highly incompressible with a bulk modulus of 307(5) GPa and a first pressure derivative of 6.2(3). *Ab initio* calculations give values ranging from 291 to 307 GPa for various carbon-ordering schemes. The ordered, orthorhombic form of Mo<sub>2</sub>C was found to be very slightly lower in energy than the disordered hexagonal phase. The calculated electronic charge distribution clearly indicates a preference for directional molybdenum–carbon bonding.

## 1. Introduction

Molybdenum hemicarbide, Mo<sub>2</sub>C, belongs to a class of technologically important, hard carbides, which also includes the carbides of titanium, chromium, zirconium, hafnium, tantalum and tungsten. Compressibility data for these materials are limited, in spite of the existence of correlations between bulk modulus and hardness [1–8]. At temperatures above 1960 °C, Mo<sub>2</sub>C adopts a disordered, hexagonal L<sup>3</sup>-type structure (space group  $P6_3/mmc$ ,  $Z = 1$ ), in which the molybdenum atoms form a hexagonal close packed array and the carbon atoms occupy one half of the octahedral interstitial sites in a random way [9, 10]. Transitions are observed to ordered superstructures upon cooling. An  $\epsilon$ -Fe<sub>2</sub>N-type structure (space group  $P\bar{3}m1$ ,  $Z = 2$ ) is present from 1960 to 1350 °C and below this temperature the structure is of the  $\zeta$ -Fe<sub>2</sub>N type (space group  $Pbcn$ ,  $Z = 4$ ). The latter is the stable structure under ambient conditions with the carbon atoms occupying one half of the octahedral sites in an ordered way. This phase is obtained by ordering the carbon atoms in the cell corresponding to the orthohexagonal (o) setting of L<sup>3</sup>-type Mo<sub>2</sub>C (h) with a doubled  $b$  parameter:  $a_o = c_h$ ,  $b_o = 2a_{2h}$ ,  $c_o = 2a_{1h} - a_{2h}$ . The structure of this form has been refined by neutron diffraction [9, 10]. In the case of x-ray diffraction, the presence of this long-range order in the carbon sublattice is extremely difficult to detect due to the very low relative scattering factor of carbon with respect to molybdenum and clear evidence of the distortion from hexagonal symmetry



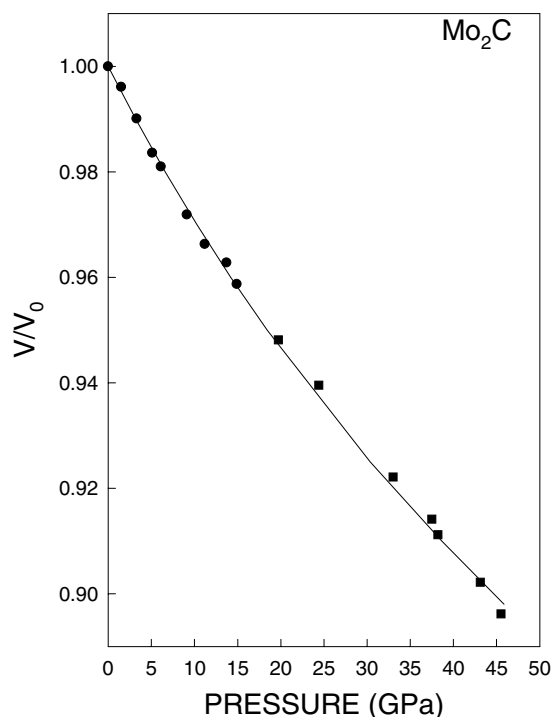
**Figure 1.** X-ray diffraction pattern of  $\text{Mo}_2\text{C}$  at 9.1 GPa. The diffraction lines of  $\text{Mo}_2\text{C}$  are indexed based on the hexagonal subcell described in the text ( $K\beta$  = the strongest  $K\beta$  reflection, which appears as a shoulder on the high angle side of the 100 reflection; Fe = diffraction lines arising from the stainless steel gasket).

is not always present in experimental x-ray diffraction patterns. In the present study, the compression behaviour of  $\text{Mo}_2\text{C}$  is investigated by x-ray diffraction and by theoretical methods and the results are compared with those of other hard materials.

## 2. Experiment

The cell constants of  $\text{Mo}_2\text{C}$  (Alpha Products, purity 99.8%) at ambient pressure were obtained using data acquired on a standard diffractometer using copper  $K\alpha$  radiation. High-pressure experiments were performed in a diamond anvil cell (DAC). Powdered  $\text{Mo}_2\text{C}$  was placed in the 150  $\mu\text{m}$  diameter hole of a stainless steel gasket preindented to a thickness of 100  $\mu\text{m}$  along with a small amount of ruby powder and 21:4:1 methanol:ethanol: $\text{H}_2\text{O}$  as a pressure transmitting medium. Pressures were measured based on the shift of the ruby  $R_1$  and  $R_2$  fluorescence lines [11]. The pressure was increased to a maximum of 15 GPa at which point the ruby  $R_1$  line was 10% broader than under ambient conditions thereby indicating the presence of nonhydrostatic stress. A second run up to 46 GPa using laser heating was thus performed; a mixture of powdered  $\text{Mo}_2\text{C}$  and NaCl was placed in the gasket hole. The NaCl served as a pressure transmitting medium and as a pressure calibrant. Pressures were measured based on the Decker equation of state of the B1 phase [12] or from the experimentally determined equation of state of the B2 phase [13]. The sample was heated before each exposure using a 50 W Nd–YAG laser in order to minimize deviatoric stress. The sample temperature was not measured, but was estimated to be over 1000  $^\circ\text{C}$  based on the visible emission observed.

Angle-dispersive, x-ray diffraction patterns were obtained on an imaging plate placed at between 113.65 and 143.62 mm from the sample using zirconium-filtered molybdenum radiation from a microfocus tube. An x-ray capillary optic was used giving a beam diameter of 100  $\mu\text{m}$ . Exposure times were typically of between 24 and 60 hours. A DAC in which the rear diamond was mounted over a  $16^\circ$  wide slit allowing access to an angular range  $4\theta = 80^\circ$  was used for these experiments. An exposure on the material recovered in the gasket after the experiment was obtained using the same installation with a sample to plate distance of 112.61 mm. The observed intensities on the imaging plates were integrated as a function of  $2\theta$  using the program X-RAY [14] in order to give conventional, one-dimensional diffraction



**Figure 2.** Relative volume of Mo<sub>2</sub>C as a function of pressure. Symbols represent data obtained below 15 GPa in a 21:4:1 methanol:ethanol:H<sub>2</sub>O medium (●) and above this value when mixed with NaCl and laser heated (■). The solid line represents a Birch–Murnaghan equation of state with  $B_0 = 307$  GPa and  $B'_0 = 6.2$ .

profiles. The individual diffraction peaks were fitted to pseudo-Voigt functions and the resulting peak positions were used in unit cell refinements with the program U-FIT [15]. All figures in parentheses refer to estimated standard deviations (esds).

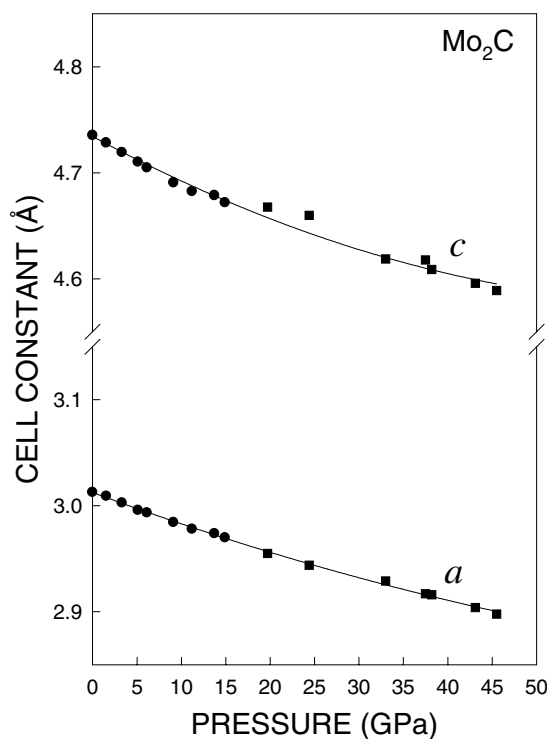
### 3. Computational procedure

Interactions between the C and Mo atoms were modelled using soft Troullier–Martins pseudopotentials [16] within the local density approximation [17, 18]. Cut-off radii were taken from Troullier and Martins [16] and Woodward *et al* [19], respectively. An appropriate cell of six or 12 atoms was employed with  $k$ -point sampling taken on a [3, 3, 3] Monkhorst–Pack grid with plane waves of cut-off energy 64 Ryd. Lattice relaxation of the parameters within the unit cell was performed using a standard technique.

## 4. Results and discussion

### 4.1. X-ray diffraction

The hexagonal cell constants of the starting Mo<sub>2</sub>C powder were  $a = 3.0128(4)$  and  $c = 4.7357(9)$  Å, which are in good agreement with literature values [20]. There was no evidence of any distortion from hexagonal symmetry. The above hexagonal cell constants correspond to a subcell of the actual orthorhombic unit cell of this stable  $\zeta$ -Fe<sub>2</sub>N-type form of Mo<sub>2</sub>C.



**Figure 3.** Cell constants of  $\text{Mo}_2\text{C}$  as a function of pressure. Symbols as for figure 2. The solid lines represent least-squares fits to the data.

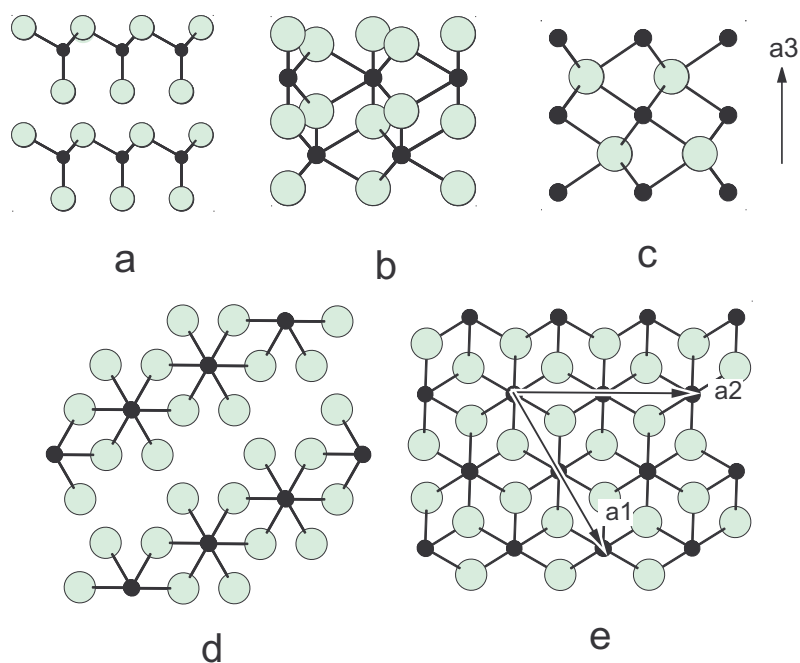
A typical x-ray diffraction pattern of  $\text{Mo}_2\text{C}$  is shown in figure 1. The 100, 002, 101, 102, 110 and 103 diffraction lines of the hexagonal subcell were used to refine the cell constants. No phase transitions were observed up to the maximum pressure of 46 GPa and the sample recovered after the experiment was found to correspond to the starting material. The experimental  $P$ – $V$  data, figure 2, were fitted using a Birch–Murnaghan equation of state [21]:

$$P = 1.5B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}][1 + 0.75(B'_0 - 4)((V/V_0)^{-2/3} - 1)]$$

where  $V_0$ ,  $B_0$  and  $B'_0$  are the volume, bulk modulus and its first derivative at ambient pressure. A bulk modulus of 307(5) GPa was obtained with  $B'_0 = 6.2(3)$ . The compression of  $\text{Mo}_2\text{C}$  is close to isotropic, figure 3, with similar initial compressibilities along  $a$  ( $\kappa_{a0} = 1.0(1) \times 10^{-3} \text{ GPa}^{-1}$ ) and  $c$  ( $\kappa_{c0} = 0.9(1) \times 10^{-3} \text{ GPa}^{-1}$ ).

#### 4.2. *Ab initio* calculations

Calculations were performed in order to determine the effect of the carbon-ordering pattern on the compressibility and the relative stability of phases and to gain an insight into the type of bonding present in  $\text{Mo}_2\text{C}$ . The calculated bulk moduli were obtained using a Birch–Murnaghan equation of state [21]. The C atoms in the  $\text{Mo}_2\text{C}$  system can be stacked in different ways. To identify the optimum stacking we have considered the possibility of four different stacking sequences shown in figure 4. The first sequence is shown in figure 4(a) and corresponds to Mo–C–Mo–Mo–C stacking where there is an empty layer of C atoms every fourth layer. This sequence was modelled using a six-atom cell and proved stable. Other sequences were



**Figure 4.** Schematic crystal structure of the configurations considered for Mo<sub>2</sub>C and discussed in the text. Larger spheres represent Mo atoms. Along the *c* direction (*a*<sub>3</sub> in the figure): Mo–C–Mo–Mo–C stacking (a), Mo–C–Mo–C stacking (b) and both the staggered and eclipsed configurations (c). In the hexagonal planes: the staggered configuration (d) and the eclipsed configuration (e).

for alternating layers in the form of Mo–C–Mo–C stacking; however to ensure correct C stoichiometry (as Mo<sub>2</sub>C) at least a 12-atom unit cell is now needed. One possible stacking is shown in figure 4(b); here there is a full Mo–C–Mo–C stacking but the four C atoms are bonded to Mo atoms along the hexagonal *c*-direction. However this form of stacking was found to be energetically far above that of the other phases in the calculational procedure and therefore has not been considered further. There are now only two other ways of enabling the Mo–C–Mo stacking, both of which appear similar when viewed along the *c*-axis as shown in figure 4(c). One possibility is a staggered configuration shown in figure 4(d) and another is an eclipsed configuration shown in figure 4(e). Of these configurations the eclipsed configuration (shown as (e)) was by far the lowest in energy and taken as the most likely candidate for the disordered hexagonal structure. The calculated 12-atom unit cell structure has atoms located at the following positions:

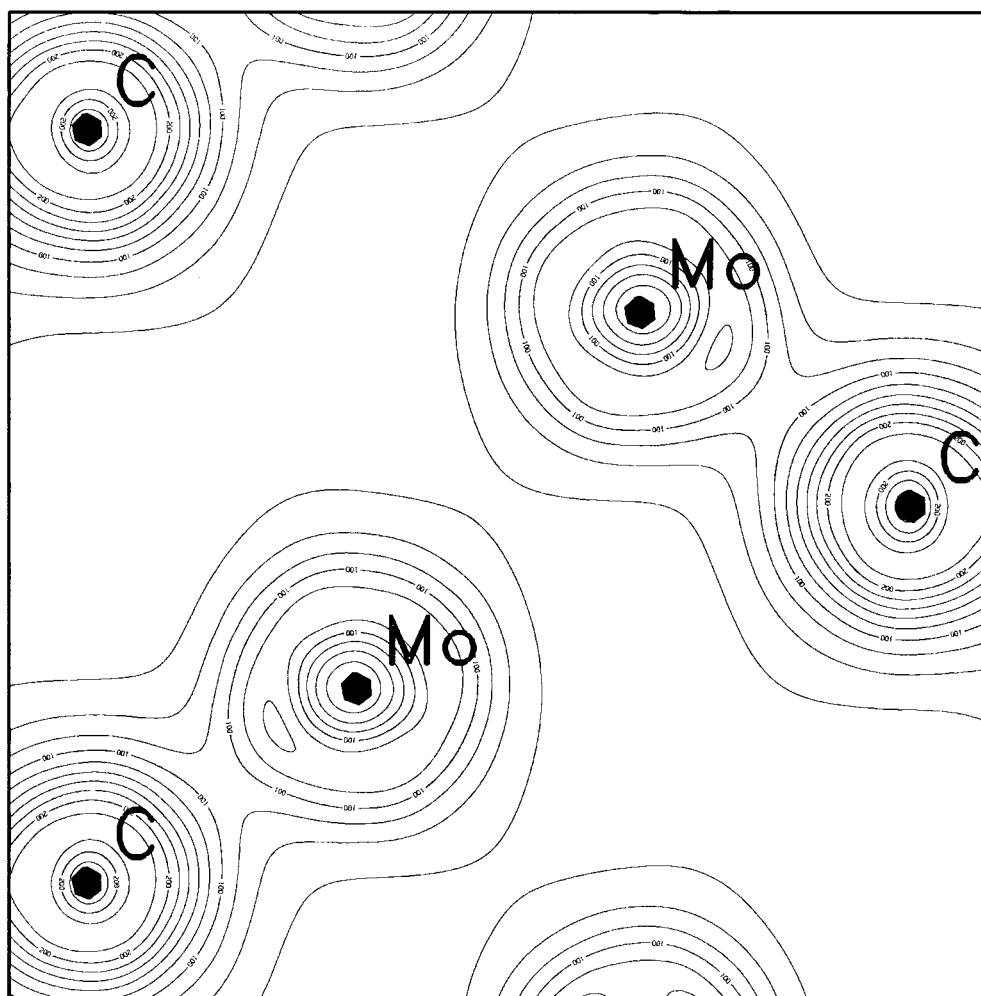
$$\begin{aligned}
 \text{C : } & (0, 0, 0) \quad (0, 1/2, 1/2) \quad (1/2, 0, 0) \quad (1/2, 1/2, 1/2) \\
 \text{Mo : } & (u, v, w) \quad (1/2 - u, 1/2 - v, 1/2 + w) \quad (u, 1/2 + v, 1/2 + w) \\
 & (1/2 - u, 1 - v, 1 - w) \quad (1/2 + u, 1/2 - v, 1/2 + w) \\
 & (1 - u, 1/2 - v, 1/2 + w) \quad (1/2 + u, 1/2 + v, 1/2 - w) \\
 & (1 - u, 1 - v, 1 - w).
 \end{aligned}$$

For overall  $P6_3/mmc$  symmetry,  $u = 1/6$ ,  $v = 1/3$ ,  $w = 1/4$ . We have considered two limiting cases in the calculations, first corresponding to no relaxation of the atoms in the unit cell and secondly where there is relaxation. Earlier in a similar study of phases of ZrO<sub>2</sub>

[22] we found that relaxation of atoms in the unit cell was needed to account for the relatively low value of the bulk modulus of the baddeleyite phase. In contrast with a similar phase of  $\text{HfO}_2$  [23] lattice relaxation was not as important. The results of the calculation for  $\text{Mo}_2\text{C}$  are given in table 1. The value of the bulk modulus is reduced by about 25% from the unrelaxed situation, whereas lattice relaxation has little effect on the cell spacing.

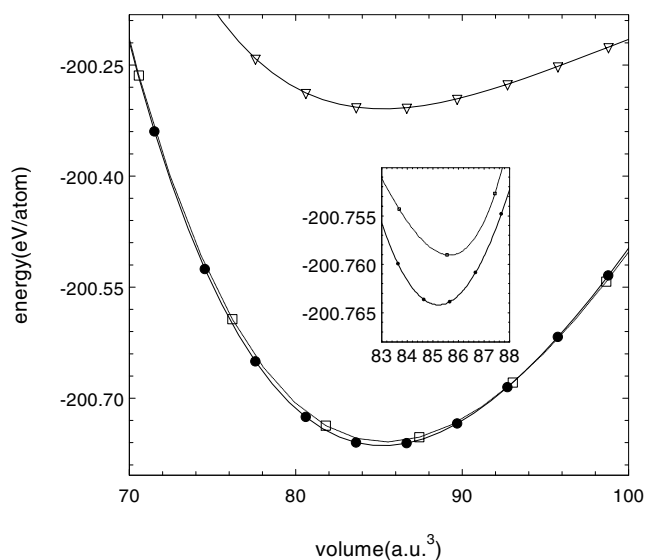
**Table 1.** Structural and compressibility data for the 12-atom hexagonal cell used for  $\text{Mo}_2\text{C}$ .

	$a$ (Å)	$c$ (Å)	$u$	$v$	$w$	$B_0$ (GPa)	$B'_0$
Unrelaxed	6.02	4.73	0.1667	0.3333	0.2500	398	4.2
Relaxed	6.02	4.74	0.1730	0.3460	0.2404	291	4.5



**Figure 5.** Charge contours in  $\text{Mo}_2\text{C}$  as viewed along the hexagonal planes. The crystallographic  $c$ -direction is vertical in the figure.

There is considerable relaxation of the Mo atoms relative to the C atoms corresponding to a movement into the vacant hexagonal lattice sites; this also results in a slight buckling



**Figure 6.** Energy as a function of volume for the orthorhombic form (●) and the staggered (▽) and eclipsed (□) hexagonal configurations of Mo<sub>2</sub>C. The very slight difference in energy between the orthorhombic and eclipsed hexagonal forms can be seen in the inset.

of the hexagonal sheets. In both cases however there is a clear indication of a directional Mo–C bond and in figure 5 we show a typical electronic structure plot of the electronic charge distribution plotted in a plane along the *c*-axis direction containing adjacent Mo and C atoms. There is a clear preference for Mo–C bonding, which indicates that Mo<sub>2</sub>C is a partially covalent compound.

Calculations were performed for the ordered orthorhombic phase of Mo<sub>2</sub>C, space group *Pbcn*, *Z* = 4. The theoretical ambient pressure cell constants (*a* = 4.735 Å, *b* = 6.125 Å, *c* = 5.260 Å) compare well with those obtained using neutron diffraction data [10] (*a* = 4.735 Å, *b* = 6.025 Å, *c* = 5.210 Å). This structure was found to be slightly lower in energy than the disordered hexagonal system described above with an energy difference of only 15 meV/formula unit, figure 6. This in agreement with the experimental observation that the orthorhombic phase is stable at ambient temperature and pressure [9, 10]. The calculations yield a bulk modulus of 307 GPa with *B*<sub>0</sub>' = 4.34. It can be noted that the bulk modulus obtained for this ordering pattern is identical to the experimental value. This value is also in close agreement with that calculated for the hexagonal phase when relaxation is permitted. The ordering pattern does thus not appear to have an important effect on the bulk modulus.

#### 4.3. Comparison with other hard materials

The present results indicate that Mo<sub>2</sub>C is among the least compressible materials. The bulk modulus of 307 GPa is only 30% lower than that of diamond, the hardest material known and which also has the highest bulk modulus (442 GPa) [24]. It is significantly less compressible than other carbides such as SiC (248 GPa) [25], TiC (235–242 GPa) [26, 27] and ZrC (223 GPa) [26] with the exception of WC (439 GPa) [28]. The hardness of Mo<sub>2</sub>C (14 GPa) [29], however, is lower than those of the above materials, which range from 24 to 30 GPa [5, 30, 31]. Molybdenum hemicarbide and tungsten carbide are similar in that their hardness values are lower than what would be expected based on correlations between bulk modulus and hardness.



It can be noted that these correlations [1–8] were established for ionic and covalent solids and that the lower than expected hardness values obtained for WC and Mo<sub>2</sub>C could be linked to a degree of metallic character which leads to a reduction in the shear strength of a material [32]. These materials are however much harder than the corresponding metals tungsten and molybdenum in agreement with the partially covalent nature of the metal–carbon bond as indicated for Mo<sub>2</sub>C in the present study.

## 5. Conclusions

The equation of state of molybdenum hemicarbide was obtained from x-ray diffraction measurements at pressures of up to 46 GPa. The compound is among the least compressible materials with a bulk modulus of 307(5) GPa. Theoretical calculations are in good agreement and give values ranging from 291 to 307 GPa depending on the carbon ordering pattern. The ordered, orthorhombic form of Mo<sub>2</sub>C was found to be very slightly lower in energy than the disordered hexagonal phase. Electronic charge distribution plots indicate the presence of directional carbon–molybdenum bonds and thus Mo<sub>2</sub>C is at least partially covalent.

## References

- [1] Goble R J and Scott S D 1985 *Can. Mineral.* **23** 273
- [2] Cohen M L 1993 *Science* **261** 307
- [3] Léger J M, Haines J and Blanzat B 1994 *J. Mater. Sci. Lett.* **13** 1688
- [4] Riedel R 1994 *Adv. Mater.* **6** 549
- [5] Sung C M and Sung M 1996 *Mater. Chem. Phys.* **43** 1
- [6] Haines J, Léger J M, Schmidt M, Petitot J P, Pereira A S and da Jornada J A H 1997 *High Pressure Research in the Biosciences and Biotechnology* ed K Heremans (Leuven: Leuven University Press) p 13
- [7] Léger J M and Haines J 1997 *Endeavour* **21** 121
- [8] Haines J and Léger J M 1998 *J. Superhard Mater.* **2** 3
- [9] Dubois J, Epicier T, Esnouf C, Fantozzi G and Convert P 1988 *Acta Metall.* **8** 1891
- [10] Epicier T, Dubois J, Esnouf C, Fantozzi G and Convert P 1988 *Acta Metall.* **8** 1903
- [11] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **B 91** 4673
- [12] Decker D L 1971 *J. Appl. Phys.* **42** 3239
- [13] Heinz D L and Jeanloz R 1984 *Phys. Rev. B* **30** 6045
- [14] Boyer J L, Hanny L, Haines J and Léger J M 1994 unpublished
- [15] Evain M 1992 *U-Fit: a Cell Parameter Refinement Program* Institut de Matériaux de Nantes
- [16] Troullier N and Martins J L 1991 *Phys. Rev. B* **43** 1993
- [17] Ceperley D M and Adler B J 1980 *Phys. Rev. B* **45** 566
- [18] Bockstede M, Kley A, Neugebauer J and Scheffler M 1997 *Comput. Phys. Commun.* **107** 187
- [19] Woodward C, Kajihara S and Young L H 1998 *Phys. Rev. B* **57** 13 459
- [20] *Powder Diffraction File Inorganic 35-787* (Swarthmore, PA: JCPDS International Center for Diffraction Data)
- [21] Birch F 1952 *J. Geophys. Res.* **57** 227
- [22] Dewhurst J K and Lowther J E 1998 *Phys. Rev. B* **57** 741
- [23] Lowther J E, Dewhurst J K, Léger J M and Haines J 1999 *Phys. Rev. B* **60** 14 485
- [24] McSkimin H J and Andreach P Jr 1972 *J. Appl. Phys.* **43** 2944
- [25] Strössner K, Cardona M and Choyke W J 1987 *Solid State Commun.* **63** 113
- [26] Chang R and Graham L J 1966 *J. Appl. Phys.* **37** 3778
- [27] Dubrovinskaia N A, Dubrovinsky L S, Saxena S K, Ahuja R and Johansson B 1999 *J. Alloys Compounds* **289** 24
- [28] Lee M and Gilmore R S 1982 *J. Mater. Sci.* **17** 2657
- [29] Thümmel F, Holleck H and Prakash L 1982 *High Temp.–High Pressures* **14** 129
- [30] Schwarzkopf P and Kieffer R 1953 *Refractory Hard Metals* (New York: Macmillan)
- [31] Teter D M 1998 *Mater. Res. Soc. Bull.* **23** 1
- [32] Haines J, Léger J M and Bocquillon G 2001 *Annu. Rev. Mater. Res.* **31** at press