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Compressibility of AlB_2 -type transition metal diborides

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Abstract

The pressure behaviour of a series of transition metal borides has been studied both experimentally and by means of *ab initio* calculations. X-ray diffraction patterns measured up to ~ 50 GPa for VB_2 and ZrB_2 show no obvious phase transition. Bulk moduli of 322 and 317 GPa, respectively, were obtained using a Murnaghan equation of state. Hartree–Fock LCCO (linear combination of crystal orbitals) calculations performed for TiB_2 have allowed its compression behaviour to be studied. The bulk modulus obtained (292 GPa) and the proposed important contribution of the interlayer interaction to the elastic behaviour under high pressure are consistent with the experimental results for the other borides.

1. Introduction

Most transition metal diborides crystallize in the simple AlB_2 -type structure (S.G. $P6/mmm$), which is usually described as a stacking of intercalated graphite-like boron sheets and hexagonal layers of the metal atoms. These compounds have been extensively studied, mainly because of the particular combination of mechanical, chemical, thermal and electrical properties [1, 2]. The recent discovery of superconductivity in MgB_2 at 39 K has reinforced the scientific importance of AlB_2 -type borides.

Despite the great interest in the understanding of the origin of all these characteristics, and the potential use of borides for high-performance applications, many of their physical properties have been little studied. Among these, their mechanical properties, mainly the high hardness, and the related behaviour under pressure are subjects which deserve more intensive investigation.

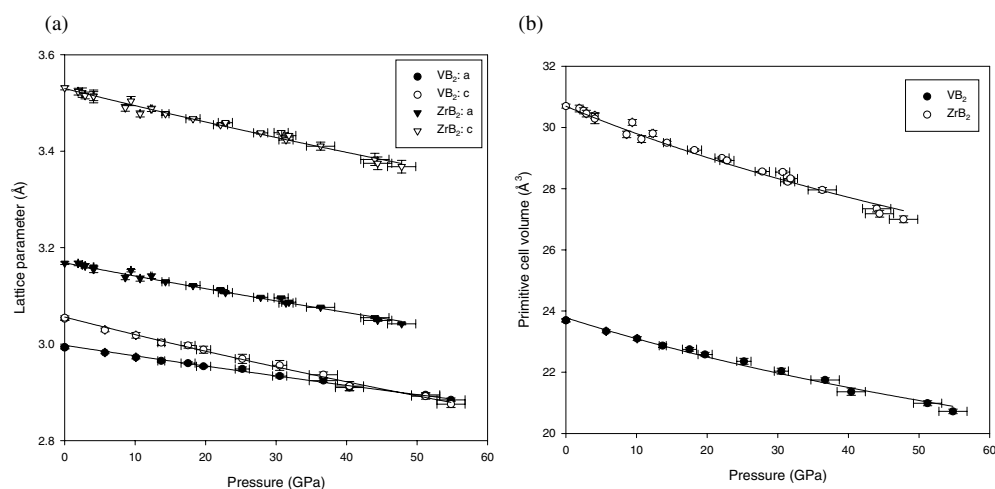


Figure 1. The pressure dependence of the experimental (a) lattice parameters and (b) unit-cell volumes for VB₂ and ZrB₂.

In this work we have studied the high-pressure behaviour of a series of borides both experimentally and by means of *ab initio* calculations. The main objectives of the experimental measurements were to investigate the phase stability under pressure of AIB₂-type structures, and to help to fill the gap in the literature regarding the values of the bulk modulus (B_0) for the diborides. The calculations have been used not only to get numerical values of B_0 and B'_0 (the first pressure derivative of B_0), but also to obtain a better picture of the compression behaviour of such compounds.

2. Experimental study

Powder samples of VB₂ and ZrB₂ (Alfa Products) were studied by means of *in situ* angle-dispersive x-ray diffraction up to ~ 50 GPa. We have used a diamond anvil cell with different kinds of gasket (tungsten, stainless steel, Inconel) and pressure-transmitting media (methanol:ethanol:water, silicon grease). The pressure was measured by the ruby fluorescence method. The diffraction patterns were obtained using a Zr-filtered Mo x-ray tube and imaging plates in a transmission geometry. At selected pressures the sample was heated using a 50 W Nd-YAG laser to minimize deviatoric stress. No associated changes in the diffraction patterns were observed.

Over the entire pressure range studied, no obvious phase transition was observed in either compound. The lattice parameters at each measured pressure were refined from conventional powder diffraction patterns obtained from integration of the observed intensities on the imaging plate. The results obtained are shown in figure 1(a), where the continuous lines are the fits of a Murnaghan-type equation of state (EOS) to the points made in order to obtain the respective inverse linear compressibilities. This procedure has given the values reported in table 1 for VB₂ and ZrB₂.

The unit-cell volume at each measured pressure (figure 1(b)) was calculated using the respective lattice parameters. The continuous curves in figure 1(b) are the fits of a Murnaghan EOS to the entire set of data shown in the figure. That EOS is the same one as is used in the computational study on TiB₂ (see the next section). The quality of the fit is similar for the range of values given in table 1. For ZrB₂ only fixed values have been used for B'_0 , because the high scatter of the experimental data prevented the use of B'_0 as a free fitting parameter.

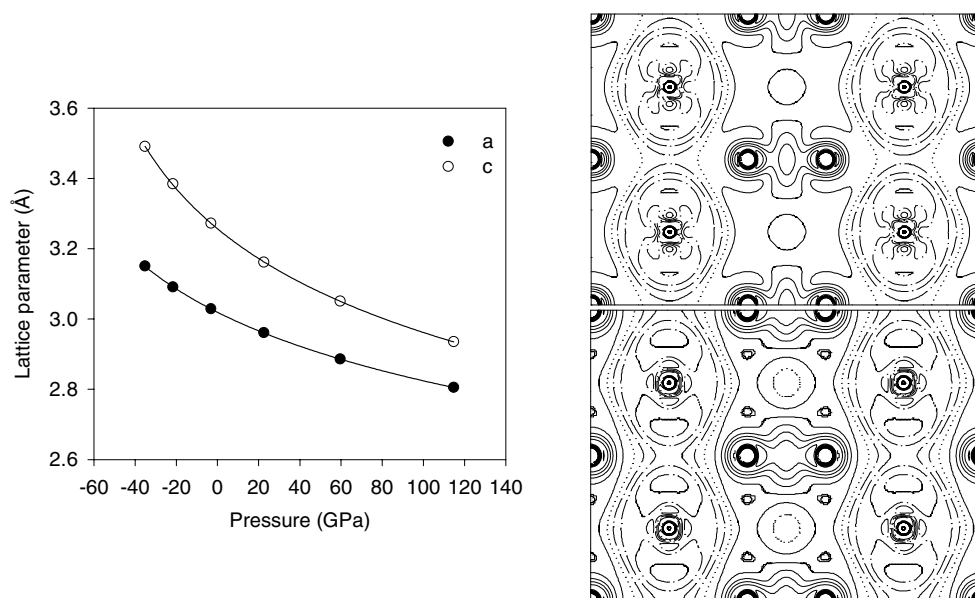


Figure 2. The pressure dependence of the calculated lattice parameters for TiB₂ (left) and the calculated electronic charge-density difference maps in the 110 plane at zero pressure (right-above) and 115 GPa (right-below). Continuous, dotted and dot-dashed curves correspond to positive, zero and negative charge density. The contours are drawn at steps of $5 \times 10^{-3} e \text{ Bohr}^{-3}$.

Table 1. The bulk moduli, the inverse linear compressibilities along the *a*- and *c*-directions and their first pressure derivatives. The *c/a* ratio at zero pressure is shown for comparison.

Boride	B_0 (GPa)	B'_0	B_{a0} (GPa)	B'_{a0}	B_{c0}	B'_{c0}	c_0/a_0
ZrB ₂ (experimental)	317 ± 7 327 ± 7 360 ± 5	4.0 (fixed) 3.34 (fixed) 1.2 (fixed)	1143 ± 18	4.0 (fixed)	955 ± 17	4.0 (fixed)	1.114
VB ₂ (experimental)	322 ± 7 333 ± 6 371 ± 18	4.0 (fixed) 3.34 (fixed) 1.2 \pm 0.9	1344 ± 20 1347 ± 73	4.0 (fixed) 3.8 \pm 3.5	813 ± 10 832 ± 38	4.0 (fixed) 3.0 \pm 1.9	1.02
TiB ₂ (calculated)	292 ± 1	3.34 ± 0.03	1031 ± 3	10.6 ± 0.2	675 ± 3	8.8 ± 0.2	1.066

3. Computational study

In order to get a better understanding of the mechanisms which determine the pressure behaviour of AlB₂-type diborides, *ab initio* calculations were performed for TiB₂ in the Hartree–Fock LCCO approximation. TiB₂ has been chosen since it is a representative member of this class of materials, and because for this compound we were able to get suitable basis functions, which allowed a structure optimization in excellent agreement with previous published results.

The calculations were performed at the athermal limit with the CRYSTAL95 code [3, 4]. The values of B_0 (= 292 GPa) and B'_0 (= 3.34) were obtained by the fitting of an integrated Murnaghan-type EOS to the total energy values calculated for optimized structures at selected unit-cell volumes [4]. The variation of the calculated lattice parameters under pressure for TiB₂ is shown in figure 2, where the continuous lines are the fits of a Murnaghan-type EOS which yields the inverse linear compressibility values reported in table 1.

4. Discussion

The results indicate that the structures studied are stable over a wide pressure range. The high values for the bulk moduli and the inverse linear compressibilities are in agreement with the high hardness of the transition metal diborides.

The experimental results show that ZrB₂ and VB₂ have essentially the same bulk modulus. However, the relative contributions from B_{a0} and B_{c0} to the resulting B_0 are quite different for each of these borides. The high value of B_{c0} for ZrB₂ indicates that compression is highly isotropic, which is not the case for VB₂. This is observed in spite of the fact that the c_0/a_0 ratio of ZrB₂ is the highest among the borides studied.

No clear volume discontinuity or abrupt change in the compressibility can be identified from the experimental results. However, any subtle effect could be masked by the intrinsically low precision in the high-pressure x-ray diffraction data. Indeed, this experimental limitation has been one of the main reasons for performing the HF calculation. We wanted to check for any evidence of a possible phase transition or a change in the compression mechanism at high pressures.

The computational calculation results for TiB₂ give no support for any abrupt change in the bulk compressibility. The calculated bulk modulus is consistent with the experimental values for the other borides. The compressibility along the c -direction is relatively high at low pressures, but it decreases strongly at higher pressures.

Another important contribution from the calculations is the electronic charge-density maps which can be plotted at different pressures. As can be seen from figure 2, there is an important charge transfer from titanium not only for regions in the boron graphite-like planes, but also to a region located in the line between boron atoms in adjacent planes. This charge transfer increases for higher pressures.

This kind of result is in agreement with a consensus view in the literature that charge transfer from metal to boron plays an important role in determining the physical properties of diborides [5]. The published results indicate that this charge transfer should increase in the sequence TiB₂ → VB₂ → ZrB₂ [6]. The same increasing sequence has been found in the present work for the values of B_{c0} .

The calculated results for TiB₂ and the high value of B_{c0} in ZrB₂ suggest the possibility of charge transfer to antibonding boron π -states with a consequent increasing in the structural rigidity along the c -direction. If this picture is confirmed by additional work, it would be very important for the understanding of the relative values of bulk and linear compressibilities in transition metal diborides.

In conclusion, we have performed an experimental and computational study of the high-pressure behaviour of transition metal diborides. The combined results indicate that interplanar interactions are important for understanding the elastic behaviour of transition metal diborides, especially at high pressure. Their compression mechanism is not that of a simple layered structure.

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