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Elastic properties of TiB_2 and MgB_2

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Abstract

We study the elastic properties, electronic structure and equation of state of titanium diboride and magnesium diboride using a first-principles pseudopotential method. We show that the results of the calculations carried out using the gradient-corrected approximation of the density-functional theory are in excellent agreement with the most recent experimental data. These results confirm that early reports of anomalously high elastic anisotropy of TiB_2 were based on erroneous experimental data for the off-diagonal components of the elastic coefficients tensor. Present results for TiB_2 are more accurate than previously reported Hartree–Fock calculations. Predicted elastic properties of the recently discovered superconductor, MgB_2 , are presented and compared to contradictory experimental estimates of bulk and linear compressibilities.

1. Introduction

1.1. Titanium diboride

TiB_2 is a member of the large family of transition metal–metalloid compounds that find numerous technological applications due to their unique physical properties. Borides as well as carbides and nitrides of transition metals are electronically conductive but are also very hard with high melting points. Traditional applications for a material like TiB_2 are based on its high strength and durability, and they are mainly limited to such areas as impact resistant armour, cutting tools, wear resistant coatings and crucibles [1, 2]. An important further development is to exploit the excellent mechanical properties of titanium diboride by incorporating TiB_2 particles in various composite materials such as particulate reinforced steel [3] or ceramic composite with titanium and boron carbides [4] or with sialons [5]. Another recently evolved application is the use of TiB_2 cathodes in the electrochemical reduction of alumina to aluminium metal [6].

Diborides, like carbides and nitrides, have very high activation energies for diffusion, because of the strong interatomic bonding, and thus resist electromigration and prevent diffusion. They therefore now find an increasing number of applications in thin-film interconnects and diffusion barriers in very large-scale integrated circuits [7]. An important advantage of diborides over carbides and nitrides is that diborides are essentially stoichiometric

and thus have much lower defect-controlled resistivity and a greater promise of industrial application in electronic devices [8]. Titanium diboride as a diffusion barrier also finds such unusual applications as a coating on particles in a bioactive glass-ceramic matrix designed for surgical implant materials [9].

Titanium diboride crystallizes in the hexagonal AlB_2 structure with the space group $P6/mmm$. There are three atoms in the unit cell, all of them on the special positions: the titanium atom at the origin and boron atoms at the $(1/3, 2/3, 1/2)$ site. The structure is thus extremely simple in that it is defined by two lattice parameters, a and c , and has a very small unit cell. Experimental estimates of the cell parameters extrapolated to 0 K give $a = 3.0236 \text{ \AA}$ and $c = 3.2204 \text{ \AA}$ [1]. A hexagonal TiB_2 crystal has six different elastic coefficients (C_{11} , C_{12} , C_{13} , C_{33} , C_{44} and C_{66}), but only five of them are independent since $C_{66} = \frac{1}{2}(C_{11} - C_{12})$.

One of the problems on the way to wider use of titanium diboride is the concern about the variability of its properties, and even insufficient knowledge of some of the fundamental material properties of TiB_2 . This paper focuses on the elastic properties that are extremely important for most applications of titanium diboride ceramic. Recent compilation of TiB_2 properties [1] covers only elastic moduli for polycrystalline samples; omission of the elastic coefficients of single crystals is unfortunate since experimental data are rare and contradictory. The main reason for the scarcity of the data is the difficulty of growing the large high-quality single crystals of TiB_2 that are required for most traditional methods. There are to the best of our knowledge only two single-crystal experimental reports. A short note on the results of ultrasonic pulse-echo measurements [10] provides four elastic coefficients and an estimate for the value of C_{13} . A more recent study [11], based on resonant ultrasound spectroscopy which does not require large samples, gives a very different set of elastic coefficients, with off-diagonal terms being an order of magnitude smaller than previously reported [10]. The new data [11] are in noticeably better agreement with the results for polycrystals [12] and thus seem to present the state-of-the-art values for the elastic coefficients of titanium diboride.

Theoretical approaches are now sufficiently accurate and efficient to help resolve such discrepancies. Nevertheless, only a few attempts to rationalize the description of elastic properties of TiB_2 based on accurate *ab initio* calculations have been described in the literature. A pseudopotential density functional (DFT) study by van Camp and van Doren [13] used a second-order expression for the energy dependence on the lattice parameters to evaluate elastic coefficients. The results of both local density approximation (LDA) and generalized gradient approximation (GGA) calculations as reported in [13] are in qualitative agreement with the latest experimental data [11]. However, only certain combinations of elastic coefficients could have been obtained using this technique as all energy points were based on calculations for the high-symmetry hexagonal phase. There is a strange result reported by van Camp and van Doren [13], namely that the equilibrium volume is smaller with the GGA than with the LDA, but nevertheless produces a smaller bulk modulus. This result is contrary to the body of available information about the relative accuracy of these two approaches: LDA calculations are generally known to produce shorter bond lengths and consequently higher bulk moduli. We thus believe that the finding of an LDA structure that is less dense and at the same time less compressible than the GGA structure [13] is erroneous.

A more recent theoretical study by Perottoni *et al* [14] used the periodic Hartree–Fock (HF) method to evaluate mechanical properties of TiB_2 . These authors used the finite-strain technique to calculate the dependence of the total energy on the applied strain and to extract elastic coefficients from the second-order fit of the obtained curves. One of the assumptions in their work was that the exact treatment of the exchange interaction in the HF technique is crucial for accurate description of charge distributions in covalent solids. They then asserted that the approximate inclusion of correlation in DFT methods does not lead to consistently better energy

derivatives, and hence does not give wholly reliable predictions of physical properties. We find this statement puzzling. The actual results quoted in [14] do not support their thesis. The agreement of HF elastic coefficients with the latest experimental data [11] is no better than in the previous DFT study [13]. Indeed, Perotoni *et al* [14] comment that there is a known tendency of HF calculations to overestimate some elastic coefficients. There is a large amount of work carried out within DFT, which illustrates the high accuracy of determination of structural parameters and physical properties of materials with various types of interatomic bonding. We earlier observed the same behaviour for another simple hexagonal system, beryllium oxide, where DFT results [15] were noticeably more accurate than the HF data [16].

The suggestion of more accurate energy derivatives in HF calculations compared to DFT cannot be substantiated by the results from [14] where neither forces nor stresses were analytically calculated within the HF approximation. The solid-state HF program used in that work does not currently support direct evaluation of the atomic forces or stresses, partly because their analytic calculation is extremely complicated in the HF formalism. Although the c/a ratio was optimized for the equation of state, effectively obtaining the stresses numerically, geometry optimization of the internal degrees of freedom was not carried out when symmetry-breaking strains were applied. It was claimed that the effect of not optimizing internal coordinates on elastic coefficients is less than 10% [14]. However, in some systems the effects can be dramatic [17], and so we believe it is always prudent to examine the role of structure optimization under strain in more detail.

1.2. Magnesium diboride

Magnesium diboride, which has the same structure as TiB₂, is substantially less studied than its titanium analogue. The recent exciting discovery of superconductivity at about 40 K in MgB₂ [18] prompted a number of experimental and theoretical studies of its properties. Experimental confirmation of the isotope effect in this compound [19] indicated that this material is likely to be a phonon-mediated BCS superconductor. This suggests that its lattice properties, and in particular compressibility, will be a subject of a great number of fundamental and applied investigations in the near future. At present there is no data on elastic coefficients of this material, and the information available on compressibility of MgB₂ is contradictory [20, 21]. It is likely that the main problem is the lack of high-quality single crystals for such measurements. We expect that the values of theoretical elastic coefficients of the ideal magnesium diboride structure will be helpful in reconciling various experimental data, as well as in the future technological applications of this material.

The aim of the present study is to provide reliable theoretical information on elastic properties of single-crystal titanium and magnesium diboride, and to shed light on the apparent controversy between the accuracy of DFT and HF results.

2. Computational details

The quantum-mechanical calculations performed here are based on density functional theory [22, 23]. Exchange–correlation effects were taken into account using the generalized gradient approximation [24], as implemented in [25]. We used the PBE form of the GGA [26], which was designed to be more robust and accurate than the original GGA formulation. Some of the calculations were repeated using the LDA exchange–correlation functional, in response to the unusual results of a previous DFT study [13]. The total energy code CASTEP [27, 28] was used, which utilizes ultrasoft pseudopotentials [29] to describe electron–ion interactions and represents electronic wavefunctions using a plane wave basis set [30].

The pseudopotentials were generated using the same exchange–correlation functional as was used in the solid state study, i.e. LDA and PBE calculations were carried out using different pseudopotentials. A purely local pseudopotential was used for magnesium [31].

One set of calculations was carried out to produce the equation of state (EOS) of titanium and magnesium diboride up to 30 GPa. Geometry optimization was performed at a fixed value of applied hydrostatic pressure, which is methodologically similar to the experimental procedure of measuring the EOS. The geometries were considered optimized when the calculated internal stress was within 0.02 GPa of the specified external stress. The calculated cell volumes were then used to construct the equation of state, which was fitted to a third-order Birch–Murnaghan equation to obtain the bulk modulus, B , and its pressure derivative, B' . The 30 GPa pressure range was chosen as representative of experimental diamond anvil cell EOS studies [32]. The response of the lattice parameters to pressure can also be fitted to a high-order polynomial, as demonstrated in [15], and thus yield values for the linear compressibilities,

$$\beta_a = -\frac{d \ln a}{dP} \quad \beta_c = -\frac{d \ln c}{dP}.$$

The second set of calculations was performed to obtain the elastic coefficients of TiB_2 and MgB_2 . Each calculation was considered converged when the maximum force on atoms in distorted structures was below $0.005 \text{ eV } \text{\AA}^{-1}$. A detailed description of the method used can be found in [15]. Two strain patterns, one with non-zero first and fourth components, and another with non-zero third component, give stresses related to all five independent elastic coefficients for the hexagonal system. Two positive and two negative amplitudes were used for each strain component with the maximum strain magnitude of 0.3%, then the elastic stiffnesses were determined from a linear fit of the calculated stress as a function of strain. The bulk modulus and linear compressibilities may also be calculated from the elastic coefficients (demonstrated in [15]), providing a method for checking the internal consistency of our calculations.

The calculations described above are not computationally expensive, because of the very small unit cells. It is thus straightforward to achieve a very high level of convergence with respect to all computational parameters. We used the plane-wave basis set defined by an energy cutoff of 400 eV. The Brillouin zone sampling was carried out using 56 k -points in the irreducible part, which corresponds to the $10 \times 10 \times 8$ set of Monkhorst–Pack points [33]. These parameters give results that should be converged with respect to the quality of the Brillouin zone integration and to the size of the basis set used, and the finite basis set correction [34] is therefore negligible. The cell parameters are converged to approximately 0.001 \AA and elastic coefficients are converged to 1 GPa with these settings.

3. Results and discussion

3.1. Equilibrium geometry and equation of state

The calculated cell parameters for both diborides are in excellent agreement with experiment and with the previous theoretical estimates as illustrated by tables 1 and 2. The uncertainty of the experimentally measured lattice parameters of MgB_2 is due to the lack of high-quality crystals of this material. It has been shown by using the atomic resolution HRTEM imaging technique that the a cell parameter can vary from 3.14 to 3.07 \AA depending on the crystal growth technique used [44]. The most reliable structure of magnesium diboride has been obtained from the low-temperature Rietveld refinement of neutron powder diffraction results [21], and our theoretical values deviate from these results by less than 0.3%.

In contrast to the earlier report [13], our LDA calculations for TiB_2 underestimate the cell parameters by 1–2% whilst still obtaining the expected high value for B . Comparison

Table 1. Theoretical and experimental data for structural parameters, bulk modulus and its pressure derivative of TiB₂; NCP—norm-conserving pseudopotentials, USP—ultrasoft pseudopotentials; HF—Hartree–Fock. The values of B and B' are evaluated from the fitting of the pressure–volume data to an analytical equation of state, and errors are obtained from the statistical analysis. Recommended theoretical results are shown in bold.

	a (Å)	c (Å)	c/a	B (GPa)	B'
USP-GGA ^a	3.0291	3.2195	1.0629	250.6(1)	3.86(1)
USP-LDA ^a	2.9905	3.1523	1.0541	277.2(3)	3.84(2)
NCP-GGA [13]	2.993	3.147	1.0515	260	
NCP-LDA [13]	3.023	3.166	1.0473	270	
HF [14]	3.027	3.240	1.0704	292	3.34
LMTO-LDA [35]	2.895	3.086 ^b	1.066 ^b	370	
TB-LMTO-LDA [36]	3.070	3.262	1.063	213	2.1
Exp. [1]	3.0236	3.2204	1.0651	237(16) ^c	2.0(2) ^c
				205(11) ^d	2.4(2) ^d
				247(12) ^e	1.9(3) ^e

^a Present results.

^b The value of c/a ratio was kept constant.

^c Ultrasonic data [37].

^d Average of shock-wave measurements on two different samples [37].

^e Shock wave data [38].

Table 2. Theoretical and experimental data for lattice parameters, linear compressibilities, bulk modulus and its pressure derivative of MgB₂; notations as in table 1.

	a (Å)	c (Å)	c/a	β_a (TPa ⁻¹)	β_c (TPa ⁻¹)	B (GPa)	B'
GGA ^a	3.073 0	3.526 6	1.147 6	1.635	3.904	139.3(3)	3.91(2)
GGA ^b	3.070 7	3.527 9	1.148 9				
GGA ^c	3.089	3.548	1.149			139(10)	
GGA ^d	3.075 4	3.526 9	1.146 8			140.1(6)	3.93(14)
Exp. [18]	3.086	3.524	1.142				
Exp. [19]	3.143 2	3.519 3	1.119 7				
Exp. [21] ^e	3.082 30(2)	3.514 61(5)	1.140 26	0.607	0.873	479	
Exp. [20]	3.090 6(2)	3.528 7(3)	1.141 8	2.4(1)	3.4(1)	120(5)	36(3)
Exp. [40]	3.085 89(1)	3.521 21(3)	1.141 8	1.85 ^f	2.73 ^f	151(5)	4 ^g
Exp. [42]	3.083	3.521	1.142				
Exp. [43]	3.084	3.523	1.142				
Exp. [44]	3.07–3.14						

^a Present results.

^b FLAPW calculations [39].

^c FLAPW calculations [40].

^d FLAPW calculations [41].

^e Measurements at 37 K.

^f Evaluated here based on the data in table 1 of [40].

^g Fixed during EOS fitting.

of our LDA and GGA results for titanium diboride shows that by applying an external hydrostatic pressure of 13 GPa while using the GGA approximation we obtain a structure that is essentially the same as the zero-pressure LDA prediction. A similar conclusion has been reached previously for hexagonal beryllium oxide, for which this ‘effective pressure’ was estimated as 14 GPa [15].

Experimental data on the TiB₂ equation of state are summarized in [37]. It appears that there are no reliable data on neither static nor shock compression of titanium diboride.

This conclusion is illustrated by the large scatter and significant error bars (see table 1) of the results quoted in [37]. It was concluded there that defects and workhardening under compression produce cusps in the shock-wave experiments. This makes analysis of the EOS data difficult and results in large scatter of the experimentally determined bulk modulus from one batch of specimens to another [37]. The reported value of the ultrasonic bulk modulus of polycrystals, 237 GPa [37], is more reliable than the shock-wave compression result. The ultrasonic bulk modulus agrees well with the present theoretical estimate of 251 GPa (table 1) and with the experimental measurement [11] obtained via single-crystal elastic coefficients, 240 GPa (table 3).

Table 3. Elastic stiffnesses of TiB₂ and MgB₂ (GPa). The bulk modulus, B , quoted here is calculated from the elastic stiffness tensor. The errors are obtained from the statistical analysis of the stress-strain results. Shear anisotropy is characterized by the ratio $A = C_{44}/C_{66}$.

Method	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	A
TiB ₂								
GGA ^a	656(2)	66(1)	98(1)	461(1)	259(1)	295(2)	250(1)	0.878
GGA ^b	655(9)	65(3)	99(2)	461(6)	260(1)	295(10)	251(2)	0.881
GGA ^c	659(10)	62(3)	100(2)	461(6)	260(1)	299(11)	251(3)	0.870
LDA ^a	709(3)	71(1)	117(1)	506(2)	295(1)	319(3)	277(1)	0.925
HF [14]	786	127	87	583	271	330	299	0.821
Ultrasonic ^d [10]	690	410	320	440	250	140	399	1.786
Ultrasonic ^d [11]	660	48	93	432	260	306	240	0.850
Ultrasonic ^e	588	72	84	503	238	258	239	0.922
Ultrasonic ^f	672	40	125	224	232	316	194	0.734
Ultrasonic ^g	711	17	118	349	240	347	237	0.692
MgB ₂								
GGA ^a	365(5)	98(5)	65(1)	203(1)	58(1)	133(5)	141(2)	0.436

^a Present results.

^b Present results, eight strain patterns up to the maximum amplitude of 2%.

^c Present results, eight strain patterns up to the maximum amplitude of 2%, no relaxation of internal degrees of freedom.

^d Single-crystal data.

^e Polycrystalline data from Manghnani *et al* as reported in [12].

^f Single-crystal elastic coefficients estimated from polycrystalline data of Manghnani *et al* in the Voight approximation [12].

^g The same as above but in the Reuss approximation [12].

Previous theoretical estimates of the bulk modulus of TiB₂, based on the DFT approach and norm-conserving pseudopotentials [13], are close to the results obtained in the present study. However, the Hartree–Fock method [14] and the all-electron LMTO–ASA technique [35] significantly overestimate the bulk modulus (table 1). The error of the LMTO calculation is especially large, both for the cell parameters and for the bulk modulus. We have to conclude that the DFT results obtained previously [35] using the LMTO–ASA technique are unreliable as far as the structure and energetics of titanium diboride are concerned. This does not diminish the importance of the analysis of the chemical bonding presented in [35]. However, more recent, accurate FLAPW calculations [45] should be preferred as a source of information about the electronic structure of this compound.

A TB–LMTO–ASA study with the LDA [36] predicted much larger cell parameters than any other theoretical work, and a correspondingly low bulk modulus. This recent study is expected to be more accurate than the earlier one [35] for at least two reasons: the use of combined correction in the ASA formalism and a much better quality of the k -point set [36]. It is thus unclear why the LDA results of the all-electron TB–LMTO calculations overestimate

the cell volume to such a degree. The most likely reason is the general shortcoming of any LMTO technique that does not contain a full-potential treatment. TB–LMTO results for the EOS parameters are also quite different from all other theoretical predictions. One possible explanation might be that a Vinet rather than Birch–Murnaghan equation of state was used in that study. However, fitting a Vinet EOS to our data gave very little difference in the fitted parameters so we conclude that the choice of EOS is not an important factor. This conclusion agrees with the results of the recent comparative study of various analytical EOS formulations which showed numerical equivalence of various equations in the moderate compression regime [46]. It is, however, possible that the results in [36] are distorted by using data points at both positive and negative pressures. Experimental results are obviously fitted for positive pressures only, which has become a standard practice in theoretical studies as well. We found that the inclusion of the tension data in the fitting procedure tends to decrease the calculated bulk modulus by up to 30%.

The pressure derivative of the bulk modulus, B' , is obtained here as 3.86 and 3.91 for TiB₂ and MgB₂, respectively. These results are close to the typical value for inorganic materials, 4.0 [47], that corresponds to the case of the validity of the second-order Murnaghan–Birch EOS. Our result for TiB₂ is noticeably higher than the reported values from both ultrasonic and shock-wave experiments (table 1) and the predicted value from the TB–LMTO–ASA study [36]. We believe that our calculated results for compressibility of titanium diboride are likely to be more accurate than the estimates obtained from shock-wave experiments.

High-pressure experimental data for MgB₂ are at present not sufficiently accurate to be used as a criterion for the validity of a theoretical study. It is well known that experimental determination of B' from the EOS is extremely challenging since it requires data of very high accuracy. Vogt *et al* [40] determined the bulk modulus from high-resolution x-ray powder diffraction measurements in a diamond anvil cell up to 8 GPa. In that work [40], the scatter of the experimental data was too high to attempt fitting to a third-order equation of state, so the first-order EOS with $B' = 4$ was used. The value of $B = 151$ GPa derived from that fit is in reasonable agreement with the theoretical result of 139 GPa. The value of 139 GPa was obtained both in the present pseudopotential study and in the all-electron FLAPW calculation [40], as shown in table 2.

Prassides *et al* [20] used a similar experimental setup to the one employed by Vogt *et al* [40] (high-resolution synchrotron x-ray diffraction, diamond anvil cell) and measured the EOS of MgB₂ up to 6 GPa. The second-order Murnaghan EOS was used to analyse the data. The reported value of $B = 120$ GPa is noticeably different from the other estimates (table 2). Even for inorganic solids with unusual bonding, it is accepted that the value of B' for inorganic solids normally lies between 3 and 7. The value of $B' = 36$ thus implies that the experimental data [20] were of very low quality and cannot be regarded as reliable.

Jorgensen *et al* [21] used a helium gas pressure cell and neutron diffraction to determine the compressibility of MgB₂ up to 0.62 GPa. This pressure range is too small to interpret the results in terms of the third-order EOS, but the bulk modulus can be evaluated from linear compressibility data. The bulk modulus of a hexagonal crystal can be written as

$$B = 1/(2\beta_a + \beta_c). \quad (1)$$

We used this relationship to evaluate the bulk modulus of MgB₂ based on the experimental results [21] for linear compressibilities (table 2). The resultant value of nearly 500 GPa is completely unrealistic and highlights the difficulty of extracting reliable elastic coefficients from low-quality compressibility data over a small pressure interval.

Equation (1) can also be used to verify the accuracy of extracting linear compressibilities from a polynomial fit to the calculated $a(P)$ and $c(P)$ curves, by comparing the bulk modulus

values thereby obtained to those derived from the third-order Birch–Murnaghan EOS (table 1). We obtained from equation (1) the values of 249 and 139 GPa for titanium and magnesium diborides, respectively, both in perfect agreement with the EOS results. Individual linear compressibilities are discussed below.

3.2. Elastic coefficients

The elastic coefficients calculated for TiB_2 and MgB_2 are presented in table 3, with values from previous theoretical and experimental work as discussed above. The consistency between our EOS and elastic coefficient calculations can be demonstrated in two ways. Firstly, the bulk modulus calculated from our elastic coefficients (table 3) agrees to better than 1 GPa with the values derived from the EOS calculation for both materials (tables 1 and 2). Secondly, the linear compressibilities calculated from the elastic coefficients and from polynomial fitting were also in excellent agreement: this comparison was presented in detail for BeO [15].

Inspection of the available sets of experimental data for elastic properties of TiB_2 (table 3) suggests that the data of Spoor *et al* [11] represent a consensus of opinion. Our GGA calculation agrees well with this set of data, while Hartree–Fock results [14] significantly overestimate most of the components of the elastic coefficients tensor. The accurate determination of the off-diagonal C_{12} component is critical for choosing between the two sets of experimental single-crystal data as presented in [10] and [11]. Our results thus strengthen the conclusion that the value of 410 GPa [10] is erroneous.

We investigated whether the overestimate of elastic coefficients in the Hartree–Fock calculations [14] was an artifact of an unsatisfactory computational protocol. In particular, we analysed the results of this calculation using the stress values produced without geometry optimization for symmetry-breaking distortions. We also extended our GGA calculations to the same maximum strain amplitude of 2% as Perotoni *et al* [14], mirroring their investigation of the higher-order terms in polynomial fits to energy as a function of strain. We found that both the structural relaxation and strain amplitude have only a minor effect on calculated elastic properties. This can be seen from the comparison of the results in the first three rows of table 3 where the difference between variously computed elastic coefficients does not exceed 4 GPa. Even for such a simple structure the effect of structural relaxation is, however, more important than that of the increased strain amplitude. We thus advocate geometry optimization as part of the procedure of computing elastic coefficients via the finite strain technique.

3.3. Anisotropy of elastic properties

It has been pointed out that the planar structure of MgB_2 and the 2D character of the covalent σ bands are likely to be responsible for its superconducting properties [48]. It is not surprising that the elastic properties of this structure are also anisotropic. The shear anisotropy ratio, $A = C_{44}/C_{66}$, is less than 0.5 and is about half that of the isostructural TiB_2 compound (table 3). This observation together with the high value of the ratio of linear compressibilities, $\beta_c/\beta_a = 2.39$, is in direct contradiction with previous conclusions of nearly isotropic mechanical behaviour of MgB_2 under pressure [40, 41]. We believe the earlier conclusions were based on a misinterpretation of the actual results. Vogt *et al* [40] and Loa and Syassen [41] interpreted small changes in c/a ratio under pressure as a sign of the isotropic nature of compression. In fact, if we were to analyse the results [40, 41] in terms of linear compressibilities β_a and β_c , the conclusions would have to be different. One can easily

show that for the hexagonal cell the difference between linear compressibilities is

$$\beta_c - \beta_a = \frac{V_0}{B} \frac{d(\ln c/a)}{dV}. \quad (2)$$

We used equation (2) to evaluate $\beta_c - \beta_a$ based on the pressure dependence of the c/a ratio [40,41] and obtained the following results: 1.31 TPa⁻¹ from FLAPW calculations [41], 1.69 TPa⁻¹ from another FLAPW study [40] and 0.91 TPa⁻¹ from low-quality experimental data [40]. The values related to the calculated FLAPW results of Vogt *et al* [40] are estimates only as they are based on the graphically presented data. Statistical reliability of the data presented in [41] is doubtful since only five theoretical points were used in the analysis of compressibility over the 40 GPa range. If one accepts a value of about 1.6 TPa⁻¹ for β_a (table 2), then the results above are consistent with the ratio of linear compressibilities of approximately two. This shows that it is not safe to assume isotropic compressibility because the c/a ratio changes by only a few per cent over a limited pressure range. In fact, these changes can correspond to twice as high compressibility in the c direction.

The value of the in-plane compressibility of MgB₂, $\beta_a = 1.64$ TPa⁻¹, is very close to that of a similar hexagonal ionic compound, BeO, where both experiment and theory agree on the value of 1.6 TPa⁻¹ [15]. Our present results for titanium diboride give a smaller, but qualitatively similar value of 1.17 TPa⁻¹. The similarity of the basal plane linear compressibilities for these two diborides supports the description of covalent B–B bonds as the strongest element of the structure. On the other hand, magnesium diboride is significantly more compressible along the c direction ($\beta_c = 3.90$ TPa⁻¹) than its titanium counterpart ($\beta_c = 1.68$ TPa⁻¹).

It was previously claimed that the accurate description of the exchange interaction in the HF scheme was necessary to properly predict the bonding and therefore, implicitly, the relative strength of TiB₂ along the normal to the basal plane [14]. Indeed, HF charge density difference maps even displayed bonding between boron atoms in different planes [14] in contrast to earlier [13] and present DFT results. We find that the nature of the bonding in these diborides can instead be simply described as covalent boron planes separated by metallic-bonded layers of Ti or Mg, respectively. There is only a weak interaction between boron atoms and metallic planes, and no indication of the B–B bonding between the layers. This conclusion is based on the analysis of DFT density-difference maps as well as on the results of Mulliken bond population calculations.

4. Conclusions

We have presented a comprehensive study of the elastic properties and equation of state of titanium and magnesium diborides. It shows that the density-functional approach produces significantly more accurate elastic coefficients than the Hartree–Fock method. The generalized gradient approximation within DFT has been shown before to efficiently and accurately reproduce the experimental elastic coefficients and to reliably predict lattice properties. This conclusion was reached, for example, while comparing DFT and HF approaches for BeO [15] and CaO [49], or DFT and empirical potential models for Al₂SiO₅ polymorphs [50].

To summarize, our results support recent data of Spoor *et al* [11] as the most accurate experimental set of elastic coefficients of TiB₂. Predicted elastic coefficients of MgB₂ are likely to be accurate to better than 10% based on the previous successful calculations for ionic and covalent crystals. We find a marked anisotropy in the mechanical properties of MgB₂, in contrast to the conclusions of previous studies that were often based on misleading methods of analysis. Further high-pressure experimental studies are required to confirm both the predicted

value of 140 GPa for the bulk modulus for magnesium diboride and the anisotropic nature of the structural changes upon compression.

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