

Elastic properties of mono- and polycrystalline hexagonal AlB_2 -like diborides of s, p and d metals from first-principles calculations

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 415218

(<http://iopscience.iop.org/0953-8984/20/41/415218>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 15:37

Please note that [terms and conditions apply](#).

Elastic properties of mono- and polycrystalline hexagonal AlB_2 -like diborides of s, p and d metals from first-principles calculations

Igor R Shein and Alexander L Ivanovskii¹

Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620041 Ekaterinburg, Russia

E-mail: ivanovskii@ihim.uran.ru

Received 16 May 2008, in final form 21 August 2008

Published 18 September 2008

Online at stacks.iop.org/JPhysCM/20/415218

Abstract

We have performed accurate *ab initio* total energy calculations using the full-potential linearized augmented plane-wave (FP-LAPW) method with the generalized gradient approximation (GGA) for the exchange–correlation potential to systematically investigate elastic properties of 18 stable, metastable and hypothetical hexagonal (AlB_2 -like) metal diborides MB_2 , where $\text{M} = \text{Na}, \text{Be}, \text{Mg}, \text{Ca}, \text{Al}, \text{Sc}, \text{Y}, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo}, \text{W}, \text{Ag}$ and Au . For monocrystalline MB_2 , the optimized lattice parameters, independent elastic constants (C_{ij}), bulk moduli (B) and shear moduli (G) are obtained and analyzed in comparison with the available theoretical and experimental data. For the first time, numerical estimates of a set of elastic parameters of the polycrystalline MB_2 ceramics (in the framework of the Voigt–Reuss–Hill approximation), namely bulk and shear moduli, compressibility (β), Young's modulus (Y), Poisson's ratio (ν) and Lamé coefficients (μ, λ), are performed.

1. Introduction

Transition metal diborides MB_2 , as well as MB_2 -based solid solutions and composites, have long attracted much attention due to their unique physical and chemical properties such as hardness, high melting point, chemical inertness etc, and belong to the most promising engineering materials with a wide range of industrial applications [1–12]. Besides bulk MB_2 materials, increasing attention has been devoted recently to their nanosized forms such as nanopowders, nanowires, nanotubes and nanocomposites [13–20].

An unexpected discovery [21] of superconductivity with the temperature of critical transition $T_C \sim 39$ K in magnesium diboride MgB_2 has given a new powerful stimulus to studying this family of materials, see reviews [22–31]. Additionally, the interest in metal diborides (such as OsB_2 , ReB_2 , RuB_2 [32–38]) has increased now due to the search for new ultra-incompressible superhard materials.

Besides the above-mentioned exciting physical properties, metal diborides also adopt several crystal structures depending on the R_M/R_B ratio, where R_M and R_B are atomic radii of metallic and boron atoms, respectively. The most representative group of MB_2 borides is formed by the layered hexagonal diborides of the AlB_2 -like structural type. For these stable AlB_2 -like MB_2 phases, the R_M/R_B ratio varies in the range from 1.14 to 2.06 [39].

Along with the above MgB_2 and AlB_2 , the best known MB_2 phases are diborides of transition metals (TMs) of IV–VI groups (Ti, Zr, Hf, Nb etc). With filling of the TM d shell, the stability of these phases rapidly decreases, and MoB_2 and WB_2 lie on the border of stability. For example, the experimental data on Mo–B phase equilibria [5, 7, 40–48] are quite contradictory: in the composition region near the ‘molybdenum diboride’ the presence of hexagonal MoB_2 , rhombohedral Mo_2B_5 , as well as the metal-deficient ($\text{Mo}_{1-x}\text{B}_2$ or $\text{Mo}_{2-x}\text{B}_5$) and boron-deficient compositions (MoB_{2-x} and $\text{Mo}_2\text{B}_{5-x}$) is reported depending on the synthetic route and the thermodynamic parameters of the process. So, the

¹ Author to whom any correspondence should be addressed.

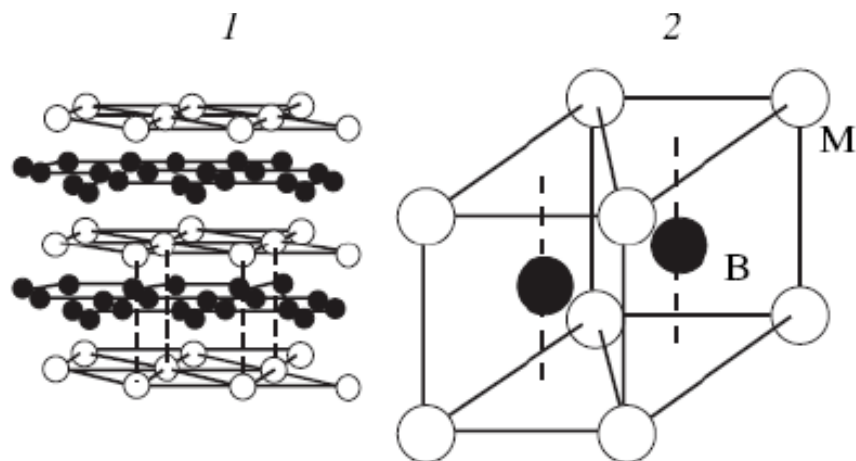


Figure 1. Crystal structure (1) and primitive cell (2) for hexagonal AlB_2 -like diborides.

products obtained [47] by mechano-chemical synthesis without external heat (MoB_2 , Mo_2B_5 or $\text{MoB}_2 + \text{Mo}_2\text{B}_5$) are strongly determined by the relation of co-milled boron and Mo powder mixtures. On the contrary, upon boronizing of Mo in molten salts [48], only the Mo_2B_5 phase was obtained.

In addition, a set of hypothetical AlB_2 -like MB_2 phases ($M = \text{Li}, \text{Na}, \text{Be}, \text{Ca}, \text{Sr}, \text{Ag}$ and Au) has recently been discussed, and their properties have been analyzed by means of theoretical approaches [26–28, 49–56]. So, some theoretical efforts have been made to predict the superconducting transition temperature T_C and the stability of these materials [26–28, 49–56]. Let us note that, despite some experimental efforts [57, 58], undoped samples of these species have not been prepared up to now.

Despite a great number of interesting results on physical properties for AlB_2 -like diborides, which have been reported in recent years, their mechanical behavior has only been sufficiently investigated for a few phases: MgB_2 , TiB_2 and ZrB_2 , whereas for the majority of other diborides these data, to our knowledge, are rather limited. Besides, most of the theoretical work devoted to the elastic behavior of MB_2 has been performed by means of different approximations and, moreover, has dealt exclusively with monocrystals. Meanwhile, the most part of the synthesized and experimentally examined MB_2 materials are polycrystalline.

In this paper, in order to get a systematic insight into the elastic properties of these materials, a comparative first-principles study of 18 AlB_2 -like diborides of I–VI groups s, p and d metals (among them there are stable: MgB_2 , AlB_2 , ScB_2 , YB_2 , TiB_2 , ZrB_2 , HfB_2 , VB_2 , NbB_2 , TaB_2 and CrB_2 , as well as metastable: MoB_2 and WB_2 , and hypothetical phases: NaB_2 , BeB_2 , CaB_2 , AgB_2 and AuB_2 , see table 1) has been performed using the FP-LAPW method within the generalized gradient approximation (GGA) for the exchange–correlation potential.

As a result, we have evaluated and analyzed a set of physical parameters of the above-mentioned MB_2 monocrystals such as optimized lattice parameters (which are obtained including the full atomic relaxations), density, elastic constants (C_{ij}), bulk modulus (B) and shear modulus (G).

Table 1. Considered hexagonal (AlB_2 -like) diborides of s, p and d metals. (Note: 1—stable, 2—metastable and 3—hypothetical MB_2 phases.)

	I	II	III	IV	V	VI
2		Be				
3	Na	Mg	Al			
4		Ca	Sc	Ti	V	Cr
5	Ag		Y	Zr	Nb	Mo
6	Au			Hf	Ta	W

1
 2
 3

Additionally, the numerical estimates of mechanical parameters: elastic modulus (B , G), compressibility (β), Young's modulus (Y), Poisson's ratio (ν) and Lamé coefficients (μ , λ) for the corresponding polycrystalline MB_2 ceramics (in the Voigt–Reuss–Hill approximation) were obtained and analyzed for the first time.

2. Method and details of calculations

The AlB_2 -like metal diborides adopt a layered crystal structure (space group $P6/mmm$), see figure 1. It is a simple hexagonal lattice of close-packed metal layers alternating with graphite-like B layers in sequence $\cdots \text{AHAAH} \cdots$ perpendicularly to the c direction [1–6]. The boron atoms are arranged at the corners of a hexagon with three nearest neighbor B atoms in each plane. The metal atoms are located at the center of the B hexagons, midway between adjacent boron layers. Thus the M and B atoms have the $[\text{MB}_{12}\text{M}_8]$ and $[\text{BM}_6\text{B}_3]$ coordination polyhedra, respectively. Each metal center has D_{6h} symmetry,

i.e. 12 borons at the vertices of a hexagonal prism. In addition, the central metal atom is coordinated also by eight metals through the faces of the B_{12} prisms. The primitive cell contains one metal and two boron atoms ($Z = 1$). There is one B and one metal in nonequivalent atomic positions of M (0, 0, 0) and B (1/3, 2/3, 1/2).

The calculations of all the mentioned diborides (table 1) were carried out by means of the full-potential method with mixed basis APW + lo (LAPW) implemented in the WIEN2k suite of programs [59]. The GGA to the exchange–correlation potential of Perdew *et al* [60] was used. The maximum value for partial waves used inside atomic spheres was $l = 12$ and the maximum value for partial waves used in the computation of muffin-tin matrix elements was $l = 4$. The plane-wave expansion with $R_{MT} \times K_{MAX}$ equal to 7, and k sampling with $10 \times 10 \times 10$ k -points mesh in the Brillouin zone was used. Relativistic effects were taken into account within the scalar-relativistic approximation. The self-consistent calculations were considered to converge when the difference in the total energy of the crystal did not exceed 0.001 mRyd as calculated at consecutive steps. Other details of the calculations are described in [46].

3. Results and discussion

3.1. Monocrystalline MB_2 phases

The equilibrium lattice constants (a and c) for all MB_2 phases are obtained from the total energy calculations, followed by the fitting of these results to the Birch–Murnaghan equation [61]. The results obtained are in reasonable agreement with the available theoretical and experimental data, table 2. The calculated ratios c/a for each MB_2 phase are also presented in table 2. According to Pearson’s criterion [79], for stable AlB_2 -like phases (see also below) the ratio c/a should lie in the interval from 0.59 to 1.2. Thus, from the data obtained it may be concluded that the diborides NaB_2 , CaB_2 , AgB_2 and AuB_2 , for which $c/a > 1.2$, should be unstable, whereas MgB_2 ($c/a = 1.15$) and YB_2 ($c/a = 1.18$) are near to the upper border of stability.

Let us discuss the mechanical parameters as obtained within the framework of the FP-LAPW–GGA calculations for MB_2 monocrystals. The values of five independent elastic constants (C_{ij} , namely C_{11} , C_{12} , C_{13} , C_{33} and C_{44} ; while $C_{66} = 1/2(C_{11}-C_{12})$) for these phases summarized in table 3 were found by imposing five different deformations (monoclinic, triclinic and three of hexagonal types, see [80]) to the equilibrium lattice of the hexagonal unit cell and by determining the dependence of the resulting energy changes on the deformation. There are some general conclusions we would like to point out from the obtained results.

Firstly, mechanically stable phases should satisfy the well-known Born criteria: $C_{11} > 0$, $(C_{11} - C_{12}) > 0$, $C_{44} > 0$ and $(C_{11} + C_{12})C_{33} - 2C_{12}^2 > 0$. In our case, these conditions are not met for four phases: BeB_2 , AgB_2 and AuB_2 , for which $C_{44} < 0$, and for NaB_2 : $(C_{11} - C_{12}) < 0$. Moreover, for all the four diborides $(C_{11} + C_{12})C_{33} - 2C_{12}^2 < 0$. This means that these hypothetical phases are mechanically

unstable. This result agrees with theoretical estimations of heats of formation for NaB_2 , BeB_2 , AgB_2 and AuB_2 [53], according to which these phases should be energetically unstable—in comparison with the mechanical mixture of the constituent reagents. Other arguments about the instability of these phases are discussed [26, 28, 51–55, 65] in terms of electronic density of states and the chemical bonding picture. Therefore, these phases will not be analyzed below.

Secondly, the estimations of the anisotropy factor $A = C_{33}/C_{11}$ (table 3) demonstrate larger elastic anisotropy in the mechanical properties for s and p metal diborides, as well as for metastable MoB_2 and WB_2 , in comparison with moderate anisotropy for other d metal diborides. Probably, this tendency may originate from strong M d–B p bonding between metal and boron sheets in these compounds, in comparison with weaker p–p and s–p bonding for s and p metal diborides, whereas for MoB_2 and WB_2 the reduction of intra-layer interactions (i.e. the growth of anisotropy) will be the result of filling of antibonding d bands [26, 28, 51–55].

The calculated elastic constants allow us to obtain the macroscopic mechanical parameters of MB_2 phases, namely their bulk (B) and shear (G) moduli. The isotropic bulk moduli B_{iso} are obtained under the assumption that the c/a ratio does not change when the lattice is subjected to isotropic stress. The relevant expression for B_{iso} [91] coincides with the definition of the bulk modulus in the Voigt (V) [92] approximation:

$$B_V = \frac{2}{9} (C_{11} + C_{12} + 2C_{13} + \frac{1}{2}C_{33}). \quad (1)$$

In the same approximation, the shear moduli (G_V) are estimated as:

$$G_V = \frac{1}{30} (C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{55} + 12C_{66}). \quad (2)$$

The results obtained are summarized in table 4 in comparison with other theoretical data. From our results we see that both bulk and shear moduli for s and p metal diborides are as a whole lower than for d metal diborides. It is usually assumed that hardness of the materials is defined by these elastic moduli: the bulk modulus is a measure of resistance to volume change by applied pressure, whereas the shear modulus is a measure of resistance to reversible deformations upon shear stress [93]. Thus, the d metal diborides are the hardest materials among all MB_2 phases.

On the other hand, according to criterion [94], a material is brittle if the B/G ratio is less than 1.75. In our case, for all the diborides, except WB_2 (for which $B/G \sim 1.9$, table 4), these parameters are much less than 1.75, i.e. these materials will behave in a brittle manner.

Finally, quite interesting conclusions follow from the comparison of our data for MB_2 phases and elastic properties of other binary phases, in particular, d metal monocarbides (MC) and mononitrides (MN), see figure 2. The comparison of our bulk modulus for MB_2 with the results [95] for MC and MN shows that the general trends in the dependence of B on the d metal type are very similar to each other. Namely: (i) the bulk modulus of all binary phases for group III metals are minimal; (ii) the bulk modulus of binary phases for III and

Table 2. Calculated lattice constants (a , c , in Å) for hexagonal (AlB₂-like) diborides of s, p and d metals in comparison with available experimental and theoretical data.

Diboride	a	c	c/a
NaB ₂	3.002	4.297	1.43
	2.995 ^a	4.229 ^a	1.41 ^a
BeB ₂	2.898	2.884	0.99
	2.89 ^a , 2.886 ^b	2.845 ^a , 3.088 ^b	0.98 ^a , 1.06 ^b
MgB ₂	3.050	3.511	1.15
	3.040 ^a , 3.080 ^b , 3.085 ^c ,	3.448 ^a , 3.532 ^b , 3.523 ^c ,	1.13 ^a , 1.15 ^b , 1.14 ^c ,
	3.098 ^d , 3.073 ^e , 3.071 ^f ,	3.520 ^d , 3.527 ^e , 3.528 ^f ,	1.14 ^d , 1.15 ^e , 1.15 ^f ,
	3.064 ^g , 3.049 ^h	3.493 ^g , 3.446 ^h	1.14 ^g , 1.13 ^h
CaB ₂	3.191	4.051	1.27
	3.183 ^a , 3.397 ^b , 3.205 ^h	4.001 ^a , 4.019 ^b , 3.974 ^h	1.26 ^a , 1.18 ^b , 1.24 ^h
AlB ₂	2.962	3.206	1.08
	2.978 ^a , 3.005 ^c , 3.008 ^l ,	3.248 ^a , 3.257 ^c , 3.261 ^l ,	1.09 ^a , 1.08 ^c , 1.08 ^l ,
	3.009 ^m , 2.998 ⁿ	3.262 ^m , 3.286 ⁿ	1.08 ^m , 1.10 ⁿ
ScB ₂	3.114	3.512	1.13
	3.114 ^a , 3.148 ^c	3.465 ^a , 3.517 ^c	1.11 ^a , 1.12 ^c
YB ₂	3.268	3.849	1.18
	3.253 ^a , 3.290 ^c	3.812 ^a , 3.835 ^c	1.17 ^a , 1.16 ^c
TiB ₂	3.006	3.212	1.07
	3.005 ^a , 3.038 ^c , 3.070 ^b ,	3.186 ^a , 3.239 ^c , 3.262 ^b ,	1.06 ^a , 1.07 ^c , 1.06 ^b ,
	3.029 ^c , 3.027 ⁱ , 2.993 ^j , 3.015 ^k	3.220 ^c , 3.240 ⁱ , 3.147 ^j , 3.222 ^k	1.06 ^c , 1.07 ⁱ , 1.05 ^j , 1.07 ^k
ZrB ₂	3.155	3.542	1.12
	3.139 ^a , 3.130 ^c , 3.127 ^o ,	3.499 ^a , 3.533 ^c , 3.523 ^o ,	1.12 ^a , 1.13 ^c , 1.13 ^o ,
	3.183 ^p , 3.169 ^q	3.546 ^p , 3.531 ^q	1.11 ^p , 1.11 ^q
HfB ₂	3.144	3.502	1.11
	3.111 ^a , 3.141 ^c	3.409 ^a , 3.470 ^c	1.10 ^a , 1.11 ^c
VB ₂	2.970	3.029	1.02
	2.969 ^a , 2.998 ^c , 3.008 ^p , 3.007 ^q	2.989 ^a , 3.005 ^c , 3.068 ^p , 3.048 ^q	1.01 ^a , 1.00 ^c , 1.02 ^p , 1.01 ^q
NbB ₂	3.086	3.318	1.08
	3.086 ^a , 3.086 ^c , 3.111 ^r , 3.181 ^q	3.304 ^a , 3.306 ^c , 3.309 ^r , 3.357 ^q	1.07 ^a , 1.07 ^c , 1.06 ^r , 1.06 ^q
TaB ₂	3.074	3.209	1.05
	3.072 ^a , 3.088 ^c , 3.164 ^q	3.275 ^a , 3.241 ^c , 3.323 ^q	1.07 ^a , 1.05 ^c , 1.05 ^q
CrB ₂	2.945	2.941	0.99
	2.970 ^a , 2.973 ^c	2.880 ^a , 3.072 ^c	0.97 ^a , 1.03 ^c
MoB ₂	3.009	3.305	1.10
	2.990 ^a , 3.039 ^c , 3.012 ^r	3.342 ^a , 3.055 ^c , 3.330 ^r	1.12 ^a , 1.05 ^c , 1.11 ^r
WB ₂	2.998	3.334	1.11
	2.972 ^a , 3.020 ^c , 3.053 ^s	3.369 ^a , 3.050 ^c , 3.306 ^s	1.13 ^a , 1.01 ^c , 1.08 ^s
AgB ₂	2.986	4.043	1.35
	2.994 ^a , 3.000 ^t , 3.034 ^u	4.051 ^a , 3.493 ^t , 4.085 ^u	1.35 ^a , 1.16 ^t , 1.35 ^u
AuB ₂	2.972	4.284	1.44
	2.982 ^a , 2.957 ^t	4.197 ^a , 3.785 ^t	1.41 ^a , 1.28 ^t

^a Reference [53], FP-LAPW + local density approximation (LDA); ^b Reference [54], tight binding-linear muffin-tin orbital method (TB-LMTO);

^c Reference [62], experiment; ^d Reference [63], FP-LAPW + generalized gradient approximation (GGA);

^e Reference [64], first-principles pseudopotential; ^f Reference [66], FP-LAPW;

^g Reference [66], density functional theory (DFT) (CRYSTAL98); ^h Reference [51], FP-LAPW + GGA;

ⁱ Reference [67], Hartree-Fock; ^j Reference [68], NCP-GGA;

^k Reference [69], Cambridge serial total energy package (CASTEP)-GGA; ^l Reference [70], plane waves-DFT;

^m Reference [71], FP-LAPW-GGA; ⁿ Reference [72], Vienna *ab initio* simulation package (VASP)-GGA;

^o Reference [73] DFT and GGA; ^p Reference [74], linear combination of atomic orbitals (LCAO)-DFT;

^q Reference [75], FP-LAPW-GGA; ^r Reference [46], FP-linear muffin-tin orbital method (LMTO);

^s Reference [76] CASTEP-LDA; ^t Reference [77], LCAO-DFT;

^u Reference [78], VASP.

IV group metals are considerably different, whereas the bulk modulus of phases for group V and VI metals are closer to each other; (iii) the bulk moduli increase for all binary phases of 3d–5d metals going from group III to VI; and (iv) in the same groups, the bulk moduli decrease going from 3d to 4d metals and increase going from 4d to 5d metals.

One noticeable difference is seen for Ta and W-based phases, where $B(\text{TaB}_2) > B(\text{WB}_2)$, whereas for the corresponding carbides and nitrides $B(\text{Ta}(\text{C}, \text{N})) < B(\text{W}(\text{C}, \text{N}))$. Obviously, this disagreement should be ascribed to the above metastability of the AlB₂-like tungsten diboride in the AlB₂-like structure because extra electrons fill the antibonding

Table 3. Calculated elastic constants (C_{ij} , in GPa) and anisotropy factors ($A = C_{33}/C_{11}$) for hexagonal (AlB₂-like) diborides of s, p and d metals in comparison with available data.

Diboride	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	A
NaB ₂	158.5	196.2	9.3	151.5	41.1	u^a
BeB ₂	358.1	255.2	114.4	106.1	-62.2	u
	696 ^b	136 ^b	88 ^b	370 ^b	119 ^b	
MgB ₂	434.8	62.1	32.8	285.4	64.4	0.65
	438 ^c , 462 ^d , 524 ^e , 431 ^f , 446 ^g , 365 ^h	43 ^c , 67 ^d , 58 ^e , 27 ^f , 68 ^g , 98 ^h	33 ^c , 41 ^d , 33 ^e , 31 ^f , 39 ^g , 65 ^h	264 ^c , 254 ^d , 243 ^e , 197 ^f , 284 ^g , 203 ^h	80 ^c , 80 ^d , 85 ^e , 85 ^f , 77 ^g , 58 ^h	
CaB ₂	237.5	97.8	34.9	289.8	96.9	1.22
AlB ₂	530.0	82.4	67.9	272.3	32.7	0.51
	665 ⁱ	41 ⁱ	17 ⁱ	417 ⁱ	58 ⁱ	
ScB ₂	508.5	41.9	73.5	373.3	189.5	0.73
YB ₂	353.9	56.6	85.9	326.7	166.3	0.92
TiB ₂	670.9	64.0	100.9	472.9	266.6	0.71
	656 ^h , 786 ^j , 588-711 ^k , 654 ^l , 671 ^m , 626 ⁿ	66 ^h , 127 ^j , 17-410 ^k , 75 ^l , 62 ^m , 68 ⁿ	98 ^h , 87 ^j , 84-320 ^k , 99 ^l , 103 ^m , 102 ⁿ	461 ^h , 583 ^j , 224-440 ^k , 443 ^l , 468 ^m , 444 ⁿ	259 ^h , 271 ^j , 232-250 ^k , 344 ^l , 269 ^m , 240 ⁿ	
ZrB ₂	540.5	55.9	111.1	422.2	252.7	0.78
	581 ^o , 596 ^p , 564-606 ^q	55 ^o , 48 ^p , 52-54 ^q	121 ^o , 169 ^p , 118-134 ^q	445 ^o , 482 ^p , 436-477 ^q	240 ^o , 240 ^p , 256-281 ^q	
HfB ₂	592.7	99.6	141.3	481.3	262.3	0.81
VB ₂	682.9	110.5	126.5	462.4	229.0	0.68
	699 ^p	146 ^p	109 ^p	552 ^p	167 ^p	
NbB ₂	608.0	104.1	193.0	493.7	220.3	0.81
	517 ^r , 290 ^s	95 ^r , 110 ^s	120 ^r , 190 ^s	528 ^r , 474 ^s	112 ^r , 225 ^s	
TaB ₂	708.6	129.2	218.6	517.0	236.6	0.73
CrB ₂	600.9	165.3	205.8	345.4	153.6	0.58
MoB ₂	621.4	116.9	228.4	404.3	175.0	0.65
WB ₂	636.1	130.0	263.4	380.9	137.1	0.60
	590-586 ^t	187-184 ^t	236-235 ^t	443-419 ^t	99-94 ^t	
AgB ₂	220.9	253.7	82.5	173.5	-42.4	u
AuB ₂	258.8	257.8	88.9	154.3	-49.4	u

^a Mechanically unstable phases, see the text.

^b Reference [81], DFT (CRYSTAL98); ^c Reference [54], TB-LMTO;

^d Reference [63], FP-LAPW + GGA; ^e Reference [82], DFT plane-wave method;

^f Reference [83], DFT; ^g Reference [84], LCAO-DFT;

^h Reference [64], first-principles pseudopotential; ⁱ Reference [70], plane waves-DFT;

^j Reference [67], Hartree-Fock; ^k Experimental data cited in [67];

^l Reference [85], FP-LAPW; ^m Reference [86], DFT-CASTEP;

ⁿ Reference [69], CASTEP-GGA; ^o Reference [28], experiment;

^p Reference [16], LCAO-DFT; ^q Reference [15], DFT (LDA-GGA);

^r Reference [87], LCAO-DFT; ^s Reference [88], CASTEP-GGA;

^t Reference [76] CASTEP (LDA-GGA).

states [26, 53]. The mentioned similarities in the changes of the bulk moduli of MB₂, MC and MN phases depending on the d metal type may seem quite surprising taking into account the fact that MB₂ and MC, MN phases adopt (i) very different structures (layered AlB₂ type *versus* isotropic B1 type) and (ii) a different nature of inter-atomic bonding (strong covalent B-B intra-layer interactions plus covalent B-M intra-layer interactions for MB₂ [26, 28, 51-55] *versus* dominant covalent M-(C, N) bonding for MC and MN [95-99]). Therefore we may suppose that the trends in elastic moduli changes for all these phases are controlled mainly by their cell volumes (i.e. atomic radii of d metals and follow the known semi-empirical expression [100-102] $B \sim 1/l^n$, where l is the bond length) and depend to a much lesser degree on the differences in structure, cohesion energies and the types of bonds in these phases (see also below).

3.2. Polycrystalline MB₂ ceramics

The above elastic parameters are obtained from first-principle calculations of MB₂ monocrystals. Meanwhile, the majority of synthesized and experimentally examined MB₂ materials are prepared and investigated as polycrystalline ceramics [1-7], i.e. in the form of aggregated mixtures of microcrystallites with a random orientation. Thus, it is useful to estimate the elastic parameters for the polycrystalline MB₂ materials.

For this purpose we utilize the Voigt-Reuss-Hill (VRH) approximation. In this approach, according to Hill [103], two main approximations, Voigt [92] and Reuss (R) [104], are used. In turn, in the Reuss model the bulk and shear moduli (B_R and G_R) are estimated as:

$$B_R = \frac{(C_{11} + C_{12})C_{33} - 2C_{12}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}} \quad (3)$$

Table 4. Calculated bulk moduli (B , in GPa) and shear moduli (G , in GPa) for monocrystalline AIB_2 -like diborides of s, p and d metals in comparison with available theoretical data.

Diboride B	G	B/G	
MgB ₂	156.7	131.5	1.19
	150 ^a , 163 ^b , 122–161 ^c , 139 ^d , 140 ^e	115 ^a , 90 ^d	
CaB ₂	122.2	111.5	1.10
	134 ^a		
AlB ₂	196.5	132.1	1.49
	195–211 ^f		
ScB ₂	196.5	202.6	0.97
YB ₂	156.7	150.0	1.05
TiB ₂	260.7	270.6	0.96
	213 ^a , 251–277 ^d , 299–306 ^g , 249–304 ^h	261 ^d , 255 ^h	
ZrB ₂	228.8	231.2	0.99
	195 ⁱ , 272–275 ⁱ , 237–260 ^k		
HfB ₂	270.0	239.9	1.17
VB ₂	283.9	246.5	1.18
	175 ⁱ , 298 ^j		
NbB ₂	298.9	219.8	1.22
	248 ^l , 298 ^m	212 ^m	
TaB ₂	340.8	243.8	1.36
CrB ₂	300.1	170.7	1.55
MoB ₂	310.5	192.0	1.62
WB ₂	329.6	171.9	1.92
	322–327 ⁿ	141–144 ⁿ	

^a Reference [54], TB-LMTO; ^b Reference [84], LCAO-DFT; ^c Reference [81], DFT (CRYSTAL98); ^d Reference [64], first-principles pseudopotential; ^e Reference [89], FP-LAPW-GGA; ^f Reference [70], plane waves-DFT; ^g Reference [67], Hartree-Fock; ^h Reference [85], FP-LAPW; ⁱ Reference [90], TB-LMTO; ^j Reference [74], LCAO-DFT; ^k Reference [73], DFT (LDA-GGA); ^l Reference [87], LCAO-DFT; ^m Reference [88], CASTEP-GGA; ⁿ Reference [76] CASTEP (LDA-GGA).

$$G_R = \frac{5}{2} \frac{[(C_{11} + C_{12})C_{33} - 2C_{12}^2] C_{55} C_{66}}{3B_V C_{55} C_{66} + [(C_{11} + C_{12})C_{33} - 2C_{12}^2] (C_{55} + C_{66})}. \quad (4)$$

Then, the Voigt and Reuss averages are limits and the actual effective moduli for polycrystals could be estimated in the VRH approach by the arithmetic mean of these two limits. In this way, when the bulk modulus (B_{VRH}) and the shear modulus (G_{VRH}) are obtained from $B_{V,R}$ and $G_{V,R}$ by the VRH approach in simple forms as $B_{VRH} = 1/2(B_V + B_R)$ and $G_{VRH} = 1/2(G_V + G_R)$, the averaged compressibility ($\beta_{VRH} = 1/B_{VRH}$) and Young's modulus (Y_{VRH}) may be calculated by the expression:

$$Y_{VRH} = \frac{9B_{VRH}G_{VRH}}{3B_{VRH} + G_{VRH}}. \quad (5)$$

Then, Poisson's ratio (ν) and the Lamé constants (μ, λ) were obtained for polycrystalline MB_2 species from B_{VRH}, G_{VRH}

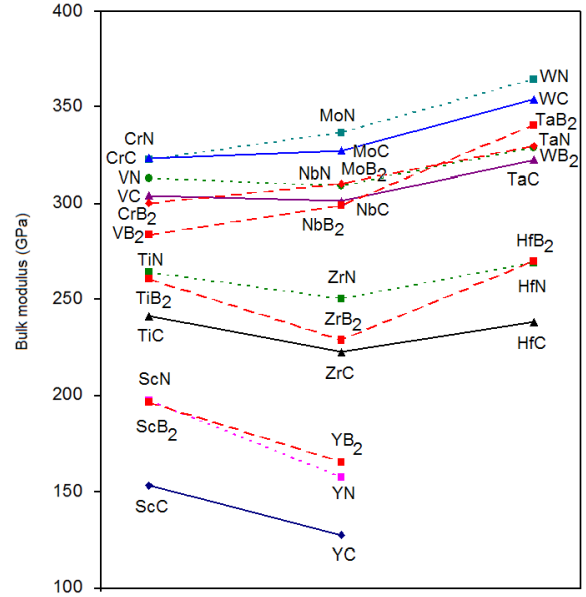


Figure 2. The calculated bulk moduli of monocrystalline AIB_2 -like diborides of 3d–5d metals in comparison with bulk moduli [95] of cubic monocarbides and mononitrides of the same metals. (This figure is in colour only in the electronic version)

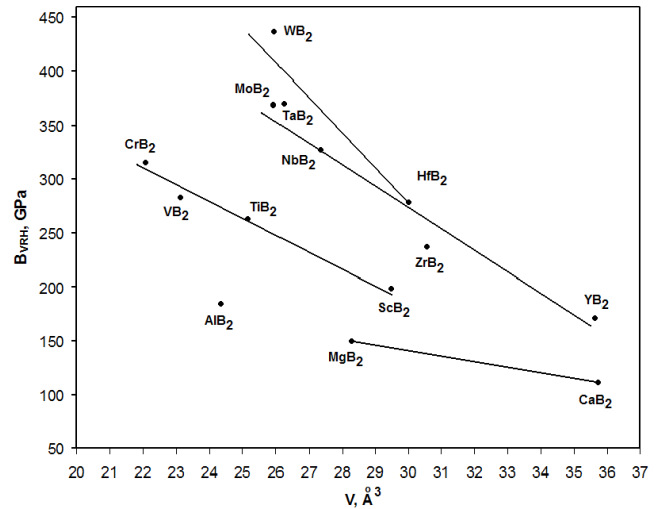


Figure 3. The calculated bulk moduli (B_{VRH} , in GPa) of polycrystalline MB_2 ceramics with respect to cell volumes of diborides.

and Y_{VRH} as:

$$\nu = \frac{3B_{VRH} - 2G_{VRH}}{2(3B_{VRH} + G_{VRH})} \quad (6)$$

$$\mu = \frac{Y_{VRH}}{2(1 + \nu)}; \quad \lambda = \frac{\nu Y_{VRH}}{(1 + \nu)(1 - 2\nu)}. \quad (7)$$

The above-mentioned parameters are summarized in table 5 in comparison with available experimental data for MB_2 ceramics. Here we should point out that our estimations are made in the limit of zero porosity of MB_2 ceramics.

It was found for the majority of MB_2 ceramics that $B_{VRH} > G_{VRH}$; this implies that the parameter limiting the

Table 5. Calculated values of some elastic parameters for MB₂ polycrystalline ceramics as obtained in the Voigt–Reuss–Hill approximation: bulk moduli (B_{VRH} , in GPa), compressibility (β , in GPa⁻¹), shear moduli (G_{VRH} , in GPa), Young's moduli (Y_{VRH} , in GPa), Poisson's ratio (ν), Lamé constant (λ , in GPa) and density (ρ , in kg m⁻³) in comparison with available experiments.

Diboride	B_{VRH}	β	G_{VRH}	Y_{VRH}	ν	λ	ρ
MgB ₂	149.9	0.006 67	117.0	278.6	0.190	71.9	2695
	145 ^a , 120 ^b , 151 ^c	0.006 90 ^a	117.5 ^a				2650 ^a
CaB ₂	111.5	0.008 97	88.9	210.7	0.185	52.2	2869
AlB ₂	184.6	0.005 41	98.2	250.2	0.274	119.3	3314
	170 ^d						3190 ^e
ScB ₂	198.9	0.005 03	201.4	451.8	0.121	64.6	3749
				480 ^f			3670 ^f
YB ₂	171.5	0.005 83	150.1	348.7	0.161	71.4	5155
TiB ₂	263.2	0.003 80	268.9	601.9	0.119	83.9	4591
	255 ^h , 276 ⁱ , 251 ^j	0.003 92 ^h , 0.003 62 ⁱ , 0.003 98 ^j	252 ⁱ , 237 ^j	372–551 ^f , 579 ^j	0.110 ^g , 0.108 ^h , 0.151 ⁱ , 0.141 ^j		4520 ^e , 4510 ⁱ , 4510 ¹⁰
		0.004 21	230.5	522.6	0.134	84.0	6135
ZrB ₂	237.6			343–506 ^e	0.110 ^e		6085 ^e , 6100 ^g
HfB ₂	278.8	0.003 59	239.5	558.6	0.166	119.2	11 078
	222 ^k			500 ^e , 497 ^k	0.120 ^g		11 190 ^e
VB ₂	283.2	0.003 53	244.1	568.8	0.165	120.5	5208
				268 ^e	0.100 ^e		5070 ^e
NbB ₂	327.3	0.003 06	221.2	541.7	0.224	179.8	6952
				637 ^e			6970 ^e
TaB ₂	370.8	0.002 70	244.0	600.3	0.230	208.2	12 814
				257 ^e			12 540 ^e
CrB ₂	315.7	0.003 17	174.2	441.5	0.267	199.6	5533
				221 ^e			5160–5200 ^e
MoB ₂	369.4	0.002 71	191.3	498.5	0.279	241.8	7533
							7780 ^e
WB ₂	436.8	0.002 29	168.8	448.7	0.329	324.3	13 150

^a Reference [106]; ^b Reference [107]; ^c Reference [108]; ^d Reference [71]; ^e Reference [109]; ^f Reference [110];

^g Reference [111]; ^h Reference [112]; ⁱ Reference [113]; ^j Reference [114]; ^k Reference [7]

stability of MB₂ materials is the shear modulus G_{VRH} . We have obtained only two deviations from this tendency: ScB₂ and TiB₂, for which $B_{\text{VRH}} \sim G_{\text{VRH}}$.

The trends of the bulk moduli for MB₂ ceramics may be discussed as displayed in figure 3. As can be seen, the bulk moduli increase as the d metal goes from group III to group VI, or downward on the periodic table; the borides of d metals have larger B_{VRH} than their s, p metal counterparts. As is seen, there is the above-mentioned distinct correlation between the elastic moduli and unit cell volumes of MB₂ phases. Generally, these trends are supported by experiment, table 5.

Thus, the diborides of s, p metals, ScB₂ and YB₂ adopt the minimal B_{VRH} , whereas the bulk moduli for the diborides of d metals of groups IV–VI may vary from 238 to 437 GPa. The maximal bulk modulus (437 GPa) and the minimal compressibility (0.002 29 GPa⁻¹) have been obtained for WB₂ ceramic. On the other hand, among group IV–VI d metal diborides, TiB₂, HfB₂, VB₂ and TaB₂ will have the maximal shear modulus ($G_{\text{VRH}} \sim 240$ – 270 GPa), i.e. the maximal bond-restoring energy under elastic shear strain, whereas according to the G_{VRH} estimations, CrB₂ ($G_{\text{VRH}} = 174$ GPa) will remain a material with the minimal hardness. The Young's modulus Y_{VRH} also the maximal and minimal values for TiB₂, HfB₂, VB₂ and TaB₂ ($Y_{\text{VRH}} \sim 560$ – 600 GPa) and CrB₂ ceramics ($Y_{\text{VRH}} = 442$ GPa), respectively.

The values of the Poisson ratio (ν) for covalent materials are small ($\nu \sim 0.1$), whereas for metallic materials ν is typically 0.33 [105]. In our case the values of ν for MB₂ vary

from about 0.120–0.166 for (Ti, Zr, Hf)B₂ to 0.267–0.310 for (Cr, Mo, W)B₂, indicating an increase of metal–metal bonding for the diborides when the d metal goes from group IV to group VI. This trend reflects the well-known situation [26–28, 53–55] when the metallicity of MB₂ phases increases with the filling of d orbitals. Finally, we have evaluated the Lamé constants, which are derived from the modulus of elasticity and Poisson's ratio (equation (7)). Physically, the first Lamé constant λ represents the compressibility of the material while the second Lamé constant μ reflects its shear stiffness. Accordingly, from our estimations (table 5) we can conclude that the maximal values of λ are received for the low-compressibility MB₂ ceramics such as WB₂, MoB₂ or TaB₂, whereas the minimal values of λ adopt the soft diborides such as CaB₂, ScB₂ and YB₂.

4. Conclusions

In summary, we have performed FP-LAPW-GGA calculations to obtain the systematic trends for elastic properties of 18 hexagonal AlB₂-like diborides of s, p and d metals, among them there are stable (MgB₂, AlB₂, ScB₂, YB₂, TiB₂, ZrB₂, HfB₂, VB₂, NbB₂, TaB₂ and CrB₂), metastable (MoB₂ and WB₂) and hypothetical phases (NaB₂, BeB₂, CaB₂, AgB₂ and AuB₂). For the first time, a set of elastic parameters of the polycrystalline MB₂ ceramics has been estimated.

Our analysis of elastic constants (C_{ij}) shows that NaB₂, BeB₂, AgB₂ and AuB₂ belong to mechanically unstable

systems. The present study reveals also that both bulk and shear moduli for s and p metal diborides are as a whole lower than for d metal diborides, i.e. d metal diborides should be the hardest materials among all the examined MB₂ phases. On the other hand, all diborides, except WB₂, will behave in a brittle manner.

From our studies of MB₂ ceramics we may draw the following main conclusions.

- (i) For the majority of diborides $B_{VRH} > G_{VRH}$, which means that a parameter limiting the stability of MB₂ materials is the shear modulus G_{VRH} .
- (ii) The values of the Poisson ratio vary from about 0.120–0.166 for (Ti, Zr, Hf)B₂ to 0.267–0.310 for (Cr, Mo, W) B₂, indicating an increase in metal–metal bonding for the diborides when d metal goes from group IV to group VI. This trend can be understood in terms of filling of the relevant d-like electronic bands.
- (iii) The bulk moduli increase as the d metal goes from group III to group VI, or downward on the periodic table; the borides of d metals have larger B_{VRH} than their s, p metal counterparts. These trends correlate with the cell volumes of MB₂ and generally are supported by experiment.

Acknowledgment

The work was supported by RFBR, grant 08-08-00034-a.

References

- [1] Lundstorm L and Rundqvist S 1965 *Borides, Silicides and Phosphides* (London: Methuen)
- [2] Post B 1964 *Refractory Binary Borides, Metallo-Boron Compounds and Boranes* (New York: Wiley)
- [3] Goldschmidt J 1967 *Interstitial Alloys* (London: Butterworths)
- [4] Samsonov G V and Vinitiskii I M 1967 *Refractory Compounds* (Moscow: Metallurgy) (in Russian)
- [5] Matkovich M I (ed) 1977 *Boron and Refractory Borides* (Berlin: Springer)
- [6] Kuzma Y B 1983 *Crystallo-Chemistry of Borides* (L'vov: L'vov University) (in Russian)
- [7] Serebriakova T I, Neronov V A and Peshev P D 1991 *High-Temperature Borides* (Moscow: Metallurgy) (in Russian)
- [8] Shveikin G P and Ivanovskii A L 1995 *Usp. Khim.* **63** 751
- [9] Mitterer C 1997 *J. Solid State Chem.* **133** 279
- [10] Ivanovskii A L and Shveikin G P 1998 *Quantum Chemistry in Material Science. Boron, Boron Compounds and Alloys* (Ekaterinburg: Ural Branch of the RAS) (in Russian)
- [11] Dahotre N B, Kadolkar P and Shah S S 2001 *Surf. Interface Anal.* **31** 659
- [12] Basu B, Raju G B and Suri A K 2005 *Int. Mater. Rev.* **51** 352
- [13] Mitterer C, Losbichler P, Warbichler P, Gibson P N and Gissler W 1998 *Vacuum* **50** 313
- [14] Ivanovskaya V V, Enyashin A N, Sofronov A A, Makurin Y N, Medvedeva N I and Ivanovskii A L 2003 *J. Mol. Struct.—Theochem* **625** 9
- [15] Ivanovskaya V V, Enyashin A N and Ivanovskii A L 2004 *Inorg. Mater.* **40** 134
- [16] Varin R A, Chiu C, Li S and Wexler D 2004 *J. Alloys Compounds* **370** 230
- [17] Shi L A, Gu Y, Chen L Y, Yang Z H and Qian Y T 2004 *Mater. Lett.* **58** 23
- [18] Jayaraman S, Klein E J, Yang Y, Kim D Y, Girolami G S and Abelson J R 2005 *J. Vac. Sci. Technol.* **23** 631
- [19] Barraud E, Begin-Colin S and LeCaer G 2005 *J. Alloys Compounds* **398** 208
- [20] Mishra S K, Rupa P K P and Pathak L C 2007 *Thin Solid Films* **17** 6889
- [21] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63
- [22] Buzea C and Yamashita T 2001 *Supercond. Sci. Technol.* **14** R115
- [23] Ivanovskii A L 2001 *Usp. Khim.* **70** 811
- [24] Canfield P C and Bud'ko S L 2002 *Phys. World* **15** 29
- [25] Ivanovskii A L, Medvedeva N I, Zubkov V G and Bamburov V G 2002 *Russ. J. Neorg. Chem.* **47** 584
- [26] Ivanovskii A L 2003 *Phys. Solid State* **45** 1829
- [27] Akimitsu J, Akutagawa S, Kawashima K and Muranaka T 2005 *Prog. Theor. Phys. Suppl.* **159** 26
- [28] Kortus J 2007 *Physica C* **456** 54
- [29] Lee S 2007 *Physica C* **456** 14
- [30] Floris A, Sanna A, Luders M, Profeta G, Lathiotakis N N, Marques M A L, Franchini C, Gross E K U, Continenza A and Massidda S 2007 *Physica C* **456** 45
- [31] Eisterer M 2007 *Supercond. Sci. Technol.* **20** R47
- [32] Cumberland R W, Weinberger M B, Gilman J J, Clark S M, Tolbert S H and Kaner R B 2007 *J. Am. Chem. Soc.* **127** 7264
- [33] Gou H Y, Hou L, Zhang J W, Li H, Sun G F and Gao F M 2006 *Appl. Phys. Lett.* **88** 221904
- [34] Chiodo S, Gotsis H J, Russo N and Sicilla E 2006 *Chem. Phys. Lett.* **425** 311
- [35] Zhou W, Wu H and Yildirim T 2007 *Phys. Rev. B* **76** 184113
- [36] Chung H Y, Weinberger M B, Levine J B, Kavner A, Yang J M, Tolbert S H and Kaner R B 2007 *Science* **316** 436
- [37] Liang Y and Zhang B 2007 *Phys. Rev. B* **76** 132101
- [38] Hao X, Wu Z, Xu Y, Zhou D, Liu X and Meng J 2007 *J. Phys.: Condens. Matter* **19** 196212
- [39] Beck P (ed) 1963 *Electronic Structure and Alloy Chemistry of the Transition Elements* (New York: Interscience–Wiley)
- [40] Higashi I, Takahashi Y and Atoda T 1976 *J. Cryst. Growth* **33** 207
- [41] Higashi I, Takahashi Y and Okada S 1986 *J. Less-Common Met.* **123** 277
- [42] Wong-Ng W, McMurdie H and Paretzkin B 1987 *Powder Diffract.* **2** 112
- [43] Okada S, Atoda T, Higashi I and Takahashi Y 1987 *J. Mater. Sci.* **22** 2993
- [44] Klesnar H, Aselage T L, Morosin B, Kwei G H and Lawson A C 1996 *J. Alloys Compounds* **241** 180
- [45] Storms E and Mueller B 1997 *J. Phys. Chem.* **81** 318
- [46] Shein I R and Ivanovskii A L 2006 *Phys. Rev. B* **73** 144108
- [47] Kudaka K, Iizumi K, Sasaki T and Okada S 2001 *J. Alloys Compounds* **315** 104
- [48] Kuznetsov S A, Kuznetsova S V, Rebrov E V, Mies M J M, de Croon M H and Schouten J C 2005 *Surf. Coat. Technol.* **195** 182
- [49] Medvedeva N I, Medvedeva J E, Ivanovskii A L, Zubkov V G and Freeman A J 2001 *JETP Lett.* **73** 336
- [50] Okatov S V, Ivanovskii A L, Medvedeva J E and Medvedeva N I 2001 *Phys. Status Solidi b* **225** R3
- [51] Medvedeva N I, Ivanovskii A L, Medvedeva J E and Freeman A J 2001 *Phys. Rev. B* **64** R020502
- [52] Satta G, Profeta G, Bernardini F, Continenza A and Massidda S 2001 *Phys. Rev. B* **64** 104507
- [53] Oguchi T 2002 *J. Phys. Soc. Japan* **71** 1495
- [54] Ravindran P, Vajeeston P, Vidya R, Kjekshus A and Fjellvag H 2001 *Phys. Rev. B* **64** 224509
- [55] Shein I R, Medvedeva N I and Ivanovskii A L 2001 *Phys. Solid State* **43** 2213

- [56] Kobayashi K, Arai M and Yamamoto K 2006 *Mater. Trans.* **47** 2629
- [57] Tomita R, Koga H, Uchiyama T and Iguchi L 2004 *J. Phys. Soc. Japan* **73** 2639
- [58] Pelleg J, Rotman M and Sinder M 2007 *Physica C* **466** 21
- [59] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties* (Vienna: Vienna Univer. Technol.)
- [60] Perdew J P, Burke S and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [61] Anderson O L 1995 *Equation of State of Solids for Geophysics and Ceramic Science* (Oxford: Oxford University Press)
- [62] Villars P 1997 *Pearson's Handbook: Crystallographic Data for Intermetallic Phases* (Materials Park, OH: ASM International)
- [63] Wang H Y, Chen X R, Zhu W J and Cheng Y 2005 *Phys. Rev. B* **72** 172502
- [64] Milman V and Warren M C 2001 *J. Phys.: Condens. Matter* **13** 5585
- [65] Kortus J, Mazin I I, Belashchenko K D, Antropov V P and Boyer L L 2001 *Phys. Rev. Lett.* **86** 4656
- [66] Islam A K M A, Islam F N and Kabir S 2001 *J. Phys.: Condens. Matter* **13** L641
- [67] Perottoni C A, Pereira A S and da Jornada J 2000 *J. Phys.: Condens. Matter* **12** 7205
- [68] van Camp P E and van Doren D E 2005 *High Pressure Res.* **13** 335
- [69] Peng F, Fu H Z and Cheng X L 2007 *Physica B* **400** 83
- [70] Liu K, Zhou X L, Chen X R and Zhu W J 2007 *Physica B* **388** 213
- [71] Mazin I I and Antropov V P 2003 *Physica C* **385** 49
- [72] Loa I, Kunc K, Syassen K and Bouvier P 2002 *Phys. Rev. B* **66** 134101
- [73] Milman V, Winkler B and Probert M I J 2005 *J. Phys.: Condens. Matter* **17** 2233
- [74] Mahmud S T, Islam A K M A and Islam F N 2004 *J. Phys.: Condens. Matter* **16** 2335
- [75] Shein I R and Ivanovskii A L 2002 *Phys. Solid State* **44** 1833
- [76] Hao X, Xu Y, Wu Z, Zhou D, Liu X, Cao X and Meng J 2006 *Phys. Rev. B* **74** 224112
- [77] Parvin F, Islam A K M A and Islam F N 2004 *Solid State Commun.* **130** 567
- [78] Shein I R, Medvedeva N I and Ivanovskii A L 2004 arXiv:cond-mat/0412426
- [79] Pearson W E 1972 *The Crystal Chemistry and Physics of Metals and Alloys* (New York: Interscience)
- [80] Shein I R, Kijko V S, Makurin Y N, Gorbunova M A and Ivanovskii A L 2007 *Phys. Solid State* **49** 1067
- [81] Islam A K M A, Islam F N, Iqbal M S, Jalbout A F and Adamowicz L 2006 *Solid State Commun.* **139** 315
- [82] Guo H Z, Chen X R, Cai L C, Zhu J and Gao J 2005 *Solid State Commun.* **134** 787
- [83] Osorio-Guillen J M, Simak S I, Wang Y, Johansson B and Aujia R 2002 *Solid State Commun.* **123** 257
- [84] Islam A K M A and Islam F N 2001 *Physica C* **363** 189
- [85] Panda K B and Ravi Chandran K S 2006 *Comput. Mater. Sci.* **35** 134
- [86] Iuga M, Steinle-Neumann G and Meinhardt J 2007 *Eur. Phys. J. B* **58** 127
- [87] Sikder A S, Islam A K M A, Nuruzzaman M and Islam F N 2006 *Solid State Commun.* **137** 253
- [88] Regalado E and Escamilla R 2007 *J. Phys.: Condens. Matter* **19** 376209
- [89] Loa I and Syassen K 2001 *Solid State Commun.* **118** 279
- [90] Vajeeston P, Ravindran P, Ravi C and Asokamani R 2001 *Phys. Rev. B* **63** 045115
- [91] Fast L, Wills J M, Johansson B and Eriksson O 1995 *Phys. Rev. B* **51** 17731
- [92] Voigt W 1928 *Lehrbuch der Kristallphysik* (Leipzig: Teubner)
- [93] Young A F, Sanloup C, Gregoryanz E, Scandolo S, Hemley R E and Mao H K 2001 *Phys. Rev. Lett.* **96** 155501
- [94] Pugh S F 1954 *Phil. Mag.* **45** 833
- [95] Isaev E I, Simak S I, Abrikosov I A, Ahuja R, Vekilov Y K, Katsnelson M I, Lichtenstein A I and Johansson B 2007 *J. Appl. Phys.* **101** 123519
- [96] Gubanov V A, Ivanovskii A L and Zhukov V P 1994 *Electronic Structure of Refractory Carbides and Nitride* (Cambridge: Cambridge University Press)
- [97] Johansson L I 1995 *Surf. Sci. Rep.* **21** 177
- [98] Stampfl C, Mannstadt W, Asahi R and Freeman A J 2001 *Phys. Rev. B* **63** 155106
- [99] Zhang Y F, Li J Q, Zhou L X and Xiang S C 2001 *Solid State Commun.* **121** 411
- [100] Cohen M L 1996 *Science* **261** 307
- [101] Cohen M L 1985 *Phys. Rev. B* **32** 7988
- [102] Kamran S, Chen K and Chen L 2008 *Phys. Rev. B* **77** 094109
- [103] Hill R 1952 *Proc. Phys. Soc. Lond. A* **65** 349
- [104] Reuss A 1929 *Z. Angew. Math. Mech.* **9** 49
- [105] Haines J, Leger J and Bocquillon G 2001 *Annu. Rev. Mater. Res.* **31** 1
- [106] Harms U, Serquis A, Schwarz R B and Nesterenko V F 2003 *J. Supercond.: Incorporating Novel Magn.* **16** 941
- [107] Prassides K, Iwasa Y, Ido T, Chi D H, Uchara K, Nishibori E, Tanaka M, Sakata M, Ohishi Y, Shimomura O, Muranaka T and Akimitsu J 2001 *Phys. Rev. B* **64** 12509
- [108] Vogt T, Schneider G, Hriljac J A, Yang G and Abell S J 2001 *Phys. Rev. B* **63** 220505
- [109] Martienssen W and Warlimont H (ed) 2005 *Springer Handbook of Condensed Matter and Materials Data* (Berlin: Springer)
- [110] Levchenko G, Lyashchenko A, Baumer V, Evdokimova A, Filippov V, Paderno Y and Shitsevalova N 2006 *J. Solid State Chem.* **179** 2949
- [111] Cutler A 1991 *Engineered Materials Handbook* vol 4 ed S J Schneider (Metals Park, OH: ASM International) p 787
- [112] Munro R G 2000 *J. Res. Natl Inst. Stand. Technol.* **105** 709
- [113] Dodd S P, Cankurtaran M, Saunders G A and James B 2001 *J. Mater. Sci.* **36** 3989
- [114] Gust W H, Holt A C and Royce E B 1973 *J. Appl. Phys.* **44** 550