Structural and mechanical stability of rare-earth diborides

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Structural and mechanical properties of several rare-earth diborides were systematically investigated by first principles calculations. Specifically, we studied XB_2, where X = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Lu in the hexagonal AlB_2, ReB_2, and orthorhombic OsB_2-type structures. The lattice parameters, bulk modulus, bond distances, second order elastic constants, and related polycrystalline elastic moduli (e.g., shear modulus, Young's modulus, Poisson's ratio, Debye temperature, sound velocities) were calculated. Our results indicate that these compounds are mechanically stable in the considered structures, and according to "Chen's method", the predicted Vickers hardness shows that they are hard materials in AlB_2- and OsB_2-type structures.

Keywords: *ab initio* calculations, elastic properties, hardness, rare-earth diborides

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1. Introduction

Ultra-hard materials are used in many applications, from cutting and polishing tools to wear-resistant coatings.[1] Unfortunately, almost all ultra-hard materials (diamond, cubic BN, etc.) are expensive because either they occur naturally only rarely or they have to be synthesized at high pressure.[2] Therefore, intense research efforts are made to design new ultra-hard materials.[1,2] Combinations of high-bulk-modulus transition metals with small, covalent bond-forming atoms such as boron, carbon, nitrogen or oxygen provide a promising approach to designing super-hard materials.[1,3]

The boron–boron bonds in the rare-earth borides containing more than 40% boron are responsible for the high hardness, high melting points, and characteristic temperatures of these materials.[4] The presence of rare-earth metals in the boride lattice leads to a wide diversity of electrical and magnetic properties.[5] The rare-earth borides such as diborides (XB_2), tetraborides (XB_4), hexaborides (XB_6), and dodecaborides (XB_{12}) have attracted a lot of attention over the years as a rich class of materials that exhibit various phenomena of f-electron magnetism.[6–11] For example, rare-earth borides possess good emissive properties and are used as cathode materials in emission electronics.[11]

A few experimental and theoretical studies of rare-earth diborides have been reported.[11–26] Yang *et al.*[12] investigated electronic properties and superconductivity of some rare-earth borides. The structural properties of SmB_2, GdB_2, HoB_2, and TmB_2 have been studied by Cannon *et al.*[13] The heat capacity of TbB_2 and DyB_2 has been experimentally measured at temperatures of 5 K–300 K by Novikov and Matovnikov.[15,16] They have also presented the total heat capacity as the sum of magnetic, lattice, and Schottky contributions. The solid state phase equilibria in the ternary *RE*–Si–B diagrams (*RE* = Gd, Dy, Ho, Er, and Y) have been determined at 1270 K using experimental techniques.[17,18] The temperature-dependent variations with lattice parameters and the thermal expansion coefficients of the rare-earth diborides RB_2 (R = Tb, Dy, Ho, Er, Tm, Lu) have been investigated in the temperature range 4.2 K–300 K.[19] LuB_2 in $P6/mmm$ structure has been synthesized[11] successfully, and the magnetic properties have been investigated by Mori *et al.*[20] Recently, we[21] reported the structural, elastic, and lattice dynamical properties of LuB_2, LuB_4, and LuB_{12} compounds. Zazoua *et al.*[24] have studied the structures and magnetic phase stability of rare-earth diboride compounds, XB_2, using density functional simulations within the local density approximation. Their results show that these compounds are incompressible materials. Very recently, the elastic constants and related moduli of these compounds (including Sm, Gd, Er, Tb, and Lu diborides) in the AlB_2-type diborides have been calculated with GGA-PBE by Duan*et al.*[28]

In the present work, we have systematically investigated the structural and elastic properties of these compounds in hexagonal AlB_2, ReB_2, and orthorhombic OsB_2-type structures. To our knowledge, elastic and thermodynamical properties, which are the important bulk properties for solids, have not been obtained either theoretically or experimentally for rare-earth diborides in ReB_2 and in OsB_2-type structures until now. The calculation method is given in Section 2; the results are discussed in Section 3. Finally, the summary and conclusion are presented in Section 4.

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2. Method of calculation

In the present work, all calculations have been carried out using the Vienna *ab-initio* simulation package (VASP)[29–31] based on density functional theory (DFT). The electron–ion interaction was considered in the form of the projector-augmented-wave (PAW) method with a plane wave energy cutoff of 450 eV.[32] This cutoff was found to be adequate for studying the structural and mechanical properties. We have not observed statistically significant changes in the key parameters when the energy cutoff is increased from 450 eV to 650 eV. For the exchange and correlation terms in the electron–electron interaction, a Perdew–Burke–Ernzerhof (PBE) type functional[33] was used within the generalized gradient approximation (GGA).

The standard PAW pseudo-potential of B was used. In the PAW method, the core electrons are replaced by an effective potential and only the remaining electrons are treated explicitly. For Sm–Lu elements, we have employed the frozen-core rare-earth pseudopotentials in which the valencies are set to 3, and the remaining f electrons spatially localized near the core are treated as core electrons. Actually, in the VASP package,[29–31] special GGA potentials are supplied for Ce–Lu, in which f electrons are kept frozen in the core (standard model for the treatment of localized f electrons). The number of f electrons in the core equals the total number of valence electrons minus the formal valency. For instance: according to the periodic table Sm has a total of 8 valence electrons (6f electrons and 2s electrons). These treatments improve the quality of pseudopotentials and can almost reproduce the results of accurate all-electron calculations that do not include a frozen core; then one can obtain the more reliable results for materials with strong magnetic moments or with atoms that have large differences in electronegativity.[34] For k-space summation the $11\times11\times11$, $8\times8\times8$, and $4\times11\times8$ Monkhorst and Pack[35] gamma centered grid of k-points have been used for AlB_2, ReB_2, and OsB_2-type structures, respectively. We have also performed several "test runs" using spin-polarizing and GGA + U approaches and compared the results obtained from standard approximation.

3. Results and discussion

3.1. Structural properties

For XB_2 within the AlB_2-type structure (space group: No. 191, $P6/mmm$), the primitive cell contains one X (rare-earth atom) and two boron atoms occupy in nonequivalent atomic positions of $1a$ (0, 0, 0) and $2d$ (1/3, 2/3, 1/2), respectively. For XB_2 within the ReB_2 type structure (space group: No. 194, $P6_3/mmc$), the two X and the four boron atoms occupy nonequivalent atomic positions of $2c$ (1/3, 2/3, 1/4) and $4f$ (2/3, 1/3, z) sites, respectively. For XB_2 within the OsB_2-type structure (Space group: No. 59, $Pmmn$), the two X and the four boron atoms occupy nonequivalent atomic positions of $2a$ (1/4, 1/4, z) and $4f$ (x, 1/4, z) sites, respectively.

First, we optimized the lattice constants and internal parameters (if available) to obtain a relaxed structure and then calculated other physical properties. The calculated bond lengths and lattice parameters are listed in Table 1 and Table 2 along with other available data for comparison. It is seen that the present lattice parameters (a, c) are in good agreement with other results.[12–14,16–28] Note that the anion atoms are the same in these compounds the cation atoms' size is different. This difference could be responsible for decreasing the lattice parameter (a) from SmB_2 to LuB_2. Typical of the rare-earth series in the structures we considered is a decrease of the lattice parameters with the atomic number, which can be interpreted as gradual localization of f electrons in the series. The calculated total energies indicate that an OsB_2-type structure is energetically favorable than other structures for SmB_2, TbB_2, DyB_2, HoB_2, ErB_2, and TmB_2 compounds. The AlB_2-type structure is energetically favorable than other structures for EuB_2, GdB_2, and LuB_2 compounds. However, in a recent study, Zazoua *et al.*,[24] using the LDA and LSDA methods, predicted that the AlB_2-type structure is more energetically favorable than other structures for these compounds. So, further study is necessary to resolve this discrepancy.

Table 1. Calculated equilibrium lattice parameters (a, and c in Å), d_{R-R}, d_{R-B}, and d_{B-B} bond distances (in unit Å) along with the available experimental and theoretical values for AlB_2 structure.

Materials	a	c	c/a	d_{R-R}	d_{R-B}	d_{B-B}	Refs.
SmB_2	3.327	4.036	1.213	3.327	2.786	1.921	present
	3.31	4.019	1.205				(LDA) Ref. [12]
	3.31	4.019	1.214				(Exp.) Ref. [13]
	3.158	4.095				1.823	(LSDA) Ref. [24]
	3.211	4.092				1.854	(LSDA + U) Ref. [24]
	3.322	4.024	1.211				(GGA) Ref. [28]
EuB_2	3.324	3.980	1.197	3.324	2.765	1.919	present
	3.198	4.056				1.846	(LSDA) Ref. [24]
	3.188	4.087				1.841	(LSDA + U) Ref. [24]

Table 1. (*Continued*).

Materials	a	c	c/a	d_{R-R}	d_{R-B}	d_{B-B}	Refs.
GdB_2	3.317	3.939	1.188	3.317	2.747	1.915	present
	3.315	3.936	1.187				(Exp.) Ref. [13]
	3.319	3.944	1.188				(Exp.) Ref. [17]
	3.236	3.883				1.868	(LSDA) Ref. [24]
	3.245	3.892				1.867	(LSDA + U) Ref. [24]
	3.310	3.940					Ref. [25]
	3.318	3.933					Ref. [27]
	3.293	3.947	1.199				(GGA) Ref. [28]
TbB_2	3.309	3.901	1.179	3.308	2.733	1.910	present
	3.28	3.86	1.177				(LDA) Ref. [12]
	3.29	3.878	1.179				(Exp.) Ref. [14]
	3.2986	3.879	1.176				(Exp.) Ref. [11]
	3.2938	3.886	1.18				(Exp.) Ref. [11]
	3.2849	3.8918	1.1848				(Exp.) Ref. [19]
	3.184	3.811				1.838	(LSDA) Ref. [24]
	3.231	3.800				1.852	(LSDA + U) Ref. [24]
	3.284	3.912	1.191				(GGA) Ref. [28]
DyB_2	3.298	3.865	1.172	3.297	2.712	1.904	present
	3.287	3.847	1.170				(LDA) Ref. [12]
	3.2858	3.8516	1.09				(Exp.) Ref. [19]
	3.292	3.852	1.17				(Exp.) Ref. [16]
	3.2902	3.8472	1.1693				(Exp.) Ref. [16]
	3.179	3.792				1.835	(LSDA) Ref. [24]
	3.213	3.822				1.847	(LSDA + U) Ref. [24]
HoB_2	3.286	3.832	1.166	3.286	2.691	1.897	present
	3.273	3.814	1.165				(LDA) Ref. [12]
	3.279	3.811	1.162				(Exp.) Ref. [13]
	3.2571	3.7597	1.1543				(Exp.) Ref. [19]
	3.281	3.816	1.163				(Exp.) Ref. [18]
	3.178	3.790				1.835	(LSDA) Ref. [24]
	3.212	3.756				1.861	(LSDA + U) Ref. [24]
	3.170	3.810					Ref. [25]
	3.281	3.811					Ref. [26]
ErB_2	3.275	3.801	1.161	3.275	2.671	1.891	present
	3.28	3.79	1.156				(LDA) Ref. [12]
	3.2681	3.783	1.158				(Exp.) Ref. [11]
	3.271	3.782	1.156				(Exp.) Ref. [11]
	3.2683	3.7810	1.1569				(Exp.) Ref. [19]
	3.265	3.770	1.155				(Exp.) Ref. [18]
	3.171	3.781				1.831	(LSDA) Ref. [24]
	3.202	3.752				1.849	(LSDA + U) Ref. [24]
	3.268	3.785	1.158				(GGA) Ref. [28]
TmB_2	3.262	3.769	1.155	3.263	2.649	1.884	present
	3.25	3.739	1.151				(LDA) Ref. [12]
	3.258	3.745	1.150				(Exp.) Ref. [13]
	3.2609	3.753	1.151				(Exp.) Ref. [11]
	3.261	3.755	1.151				(Exp.) Ref. [11]
	3.2548	3.7549	1.1536				(Exp.) Ref. [19]
	3.26	3.754	1.151				(Exp.) Ref. [20]
	3.257	3.747	1.150				(Exp.) Ref. [22]
	3.261	3.755	1.152				(Exp.) Ref. [23]
	3.171	3.767				1.831	(LSDA) Ref. [24]
	3.153	3.850				1.820	(LSDA + U) Ref. [24]
	3.254	3.761	1.156				(GGA) Ref. [28]
LuB_2	3.242	3.717	1.146	3.242	2.615	1.872	(GGA) Ref. [21].
	3.241	3.698	1.141				(LDA) Ref. [12]
	3.244	3.704	1.142				(Exp.) Ref. [20]
	3.2412	3.701	1.142				(Exp.) Ref. [11]
	3.246	3.704	1.141				(Exp.) Ref. [11]
	3.181	3.641				1.839	(LDA) Ref. [24]
	3.183	3.630					(LDA(os)) Ref. [24]
	3.242	3.73	1.151				(GGA) Ref. [28]

Table 2. Calculated equilibrium lattice parameters (a, b, and c in unit Å), d_{X-X}, d_{X-B}, and d_{B-B} bond distances (in Å) along with the available experimental and theoretical values for ReB_2 and OsB_2 structures.

Structure	Materials	a	c	c/a	d_{X-X}	d_{X-B}	d_{B-B}
ReB_2	SmB_2	4.507	6.765	1.5	4.268	2.607	1.5518
	EuB_2	4.461	6.736	1.51	4.239	2.592	1.553
	GdB_2	4.424	6.709	1.516	4.216	2.577	1.5543
	TbB_2	4.391	6.684	1.522	4.195	2.564	1.5553
	DyB_2	4.359	6.661	1.528	4.175	2.553	1.5563
	HoB_2	4.329	6.641	1.534	4.156	2.542	1.5575
	ErB_2	4.301	6.624	1.54	4.139	2.533	1.5587
	TmB_2	4.27	6.606	1.546	4.122	2.523	1.5603
	LuB_2	4.22[a]	6.572[a]	1.557[a]	4.091[a]	2.505[a]	1.5628[a]
Structure	Materials	a	b	c	d_{X-X}	d_{X-B}	d_{B-B}
OsB_2	SmB_2	7.154	3.156	3.788	3.91	2.743	1.626
	EuB_2	7.012	3.157	3.763	3.845	2.719	1.633
	GdB_2	6.909	3.156	3.741	3.798	2.701	1.639
	TbB_2	6.797	3.156	3.724	3.747	2.684	1.646
	DyB_2	5.710	3.294	3.871	3.296	2.716	1.904
	HoB_2	5.692	3.283	3.838	3.285	2.7	1.898
	ErB_2	5.674	3.272	3.805	3.275	2.684	1.891
	TmB_2	5.653	3.260	3.772	3.263	2.667	1.884
	LuB_2	5.619	3.240	3.720	3.243	2.64	1.872

[a] GGA taken from Ref. [21].

The phase transition pressure of these compounds is obtained from the equation of state data where the phase transition occurs once the enthalpy difference of the two phases becomes zero.

Our results show that the compounds EuB_2, GdB_2, TbB_2, ErB_2, and LuB_2, all energetically favorable in an AlB_2-type structure, do not undergo any structural phase transition, but DyB_2, HoB_2, and TmB_2 exhibit structural phase transitions at 39.8, 39.0, and 43.3 GPa, respectively. The SmB_2 compound easily transforms from OsB_2 to AlB_2-type structure under small pressure (1.47 GPa).

3.2. Elastic properties

The elastic constants of solids provide a link between the mechanical and dynamical behaviors of crystals and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials, and their *ab-initio* calculations require precise methods. Since the forces and elastic constants are functions of the first-order and second-order derivatives of the potentials, their calculation will provide a further check on the accuracy of the calculation of forces in solids.

We have used the "stress-strain" relations to compute the elastic constants,[36] and the findings are given in Tables 3 and 4 along with the other published data for comparison. The deviation from others' results[24,28] for the elastic constants of the AlB_2 structure may stem from different calculation techniques, pseudopotential or exchange–correlation potential used. Unfortunately, there are no theoretical or experimental results for ReB_2 and OsB_2-type structures to compare with the present work. So our results can serve as a prediction for future investigations. All of the studied compounds with hexagonal and orthorhombic structures satisfy Born's stability criteria; hence they are all mechanically stable. The magnitudes of elastic constants (C_{11}, C_{44}, C_{33}, and C_{66}) are consistent with the trend of increase in atomic number for AlB_2 and ReB_2-type structures.

Table 3. The calculated elastic constants (C_{ij} in GPa) for an AlB_2 structure.

Materials	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C^*_{66}	Refs.
SmB_2	283	34.4	80.2	300.4	146.8	124.3	present
	282.9	34.4	80.2	300.3	146.8	124.3	GGA+S
	237.98	110.77	90.13	280.35	196.7	63.6	LSDA[a]
	340.56	64.41	109.27	436.57	200.37	138.08	LSDA + U[a]
	236	53	75	302	142		GGA[b]
EuB_2	308.5	31.4	81.6	312.6	152.3	138.5	present
	237.98	110.77	90.13	280.35	196.7	63.6	LSDA[a]
	211.35	103.5	79.13	249.18	129.52	53.93	LSDA + U[a]
GdB_2	329.6	31.7	80.8	319.7	156.1	148.9	present
	261.84	128.9	102.32	342.5	195.18	66.47	LSDA[a]
	294.45	98.49	92.5	333.15	197.25	97.98	LSDA + U[a]
	246	55	75	284	131		GGA[b]
TbB_2	356.7	33.8	82.6	329.5	159.7	161.5	present
	299.25	96.93	110.92	354.25	219.25	101.16	LSDA[a]
	243.56	44.07	122.83	370.47	212.46	99.74	LSDA + U[a]
	252	53	72	289	125		GGA[b]
DyB_2	381.3	36.3	83.4	338.5	162.9	172.5	present
	293.94	89.96	83.02	343.57	214.13	101.99	LSDA[a]
	353.8	96.43	103.63	377.14	227.09	128.69	LSDA + U[a]
HoB_2	395.7	37.5	81	344.2	165.9	179.1	present
	324.33	99.73	46.31	447.68	198.1	112.3	LSDA[a]
	337.79	121.08	90.29	383.44	208.32	108.36	LSDA + U[a]
ErB_2	407.7	38	79	349.5	169.2	184.8	present
	320.01	107.38	81.51	344.39	199.45	106.31	LSDA[a]
	328.77	88.97	75.23	341.04	225.24	119.9	LSDA + U[a]
	287	52	73	267	127		GGA[b]
TmB_2	420.5	38.7	77.8	355	172.6	190.9	present
	322.02	111.76	83.1	314.54	193.65	105.13	LSDA[a]
	376.47	84.56	30.21	312.21	247.17	145.95	LSDA + U[a]
	301	52	64	275	123		GGA[b]
LuB_2	441.5	40.8	75.6	362.4	176.4	200.3	GGA[c]
	412.54	125.14	91.23	398.9	234.2	143.7	LDA[a]
	434	52	72	354	169		GGA[b]

* $C_{66} = (C_{11} - C_{12})/2$.

[a] Theoretical LSDA and LSDA + U results taken from Ref. [24].

[b] GGA results taken from Ref. [28].

[c] GGA results taken from Ref. [21].

Table 4. The calculated elastic constants (C_{ij} in unit GPa) for ReB_2 and OsB_2 structures.

Structure	Materials	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}			
ReB_2	SmB_2	104.6	38.2	21	279.8	14.1	33.2			
	EuB_2	109.4	40.1	19.7	294.3	14.7	34.6			
	GdB_2	112.4	41.7	18.3	304.9	15.1	35.3			
	TbB_2	115.8	43.4	16.9	315.3	15.4	36.2			
	DyB_2	118.6	44.8	16.5	322.7	15.7	36.9			
	HoB_2	121.2	46	16.7	328	15.9	37.6			
	ErB_2	123.8	47.1	16.7	333.5	16.1	38.4			
	TmB_2	127.3	48.5	16.2	341.5	16.3	39.4			
	LuB_2	133.0[a]	50.8[a]	14.1[a]	358.5[a]	16.4[a]	41.1[a]			
Structure	Materials	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
OsB_2	SmB_2	168.8	49.9	87.3	470	7.6	209.8	53.8	110.1	85.4
	EuB_2	178.7	50	90.3	476.6	9.7	224.1	64.6	119	94.7
	GdB_2	186.6	48.9	92.3	484.6	10.4	232.7	70.9	124.3	103.9
	TbB_2	190.6	53.5	95.7	483.2	12.3	241.8	76.6	129.9	114.6
	DyB_2	375.8	35.2	85.7	372.8	88.1	335.3	162.9	161	170.4
	HoB_2	391.9	36	83	386.7	87.4	340.1	165.8	163.8	177.1
	ErB_2	405.2	36.2	80.4	397.5	86.3	344.3	169.1	167	182.6
	TmB_2	419.8	36.6	78.2	410.2	85.7	349.4	172.5	170.3	188.7
	LuB_2	442.4	37.7	74.3	431.4	83.2	356.1	175.9	173.7	198.2

[a] GGA taken from Ref. [21].

The elastic constants C_{11} and C_{33} measure the a- and c-direction resistance to linear compression, respectively. The present C_{11} is higher than the C_{33} for TbB_2, DyB_2, HoB_2, ErB_2, TmB_2, and LuB_2 in the AlB_2 structure. Thus, the c axis is more compressible than the a axis for these compounds. In the ReB_2 structure, C_{33} is higher than C_{11} for all compounds. For the OsB_2 structure, C_{33} is higher than C_{11} for SmB_2, EuB_2, GdB_2, and TbB_2 compounds. Therefore, the a axis is more compressible than the c axis. In all materials, the highest values of C_{11} (442.4 GPa) and C_{33} (362.4 GPa) are those for LuB_2. We have also performed several test runs using spin-polarized and GGA + U, U values taken from Ref. [24], and compared the results with the standard approximation. The elastic constants calculated by taking into account the spin polarizing effect for SmB_2 are also tabulated in Table 3. We have not observed any significant difference in results and decided to use only a "standard approximation" without spin polarizing and $+U$ effects.

It is known that the elastic constant C_{44} is the most important parameter indirectly governing the indentation hardness of a material. A large C_{44} means a strong ability to resist monoclinic shear distortion in the (100) plane, and C_{66} relates to the resistance to shear in the $\langle 110 \rangle$ direction. In the present case, C_{44} and C_{66} are higher for LuB_2 than those for the other compounds in each structure.

The bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) are the most interesting elastic properties for applications. They are often measured for polycrystalline materials while investigating their hardness. Young's modulus and Poisson's ratio have been calculated in terms of the computed data by using the relation given in Ref. [37]. The bulk and isotropic shear moduli have been calculated with the Voigt–Reuss–Hill approximation.[38] These quantities are given in Tables 5 and 6 along with the other published results for comparison.

Bulk modulus is a measure of the resistance of a solid to volume change. The ReB_2 structure has a higher cell volume than AlB_2 and OsB_2 structures, which may result in the lower bulk moduli of the ReB_2 structure. The bulk moduli indicate that LuB_2 is the least compressible material in all structures. The shear modulus, a measurement of resistance to shape change, is more pertinent to hardness, and a larger shear modulus is mainly due to a larger C_{44}. The calculated shear modulus of these compounds for the AlB_2-type structure is higher than for the ReB_2 and OsB_2-type structures, and LuB_2 in the AlB_2 structure possesses the largest shear modulus among these compounds.

Young's modulus is defined as the ratio of stress and strain, and serves as a measure of the stiffness of the solid. When E is large, the material is stiff. In this context, due to the higher Young's modulus (404.8 GPa), LuB_2 in the AlB_2 structure is stiffer than the other compounds. If the value of E, which has an impact on ductility, increases, the covalence of the material also increases. From Tables 5 and 6, one can see that E increases as we move across $SmB_2 \rightarrow LuB_2$ for these structures.

Table 5. The calculated isotropic bulk modulus (B in unit GPa), shear modulus (G in unit GPa), Young's modulus (E in unit GPa), Poisson's ratio (ν), hardness (H in unit GPa), Debye Temperature (Θ_D in unit K), and sound velocity (v_l, v_t, and v_m in unit m/s) for AlB_2 structure.

	B	B_{eos}	G	E	ν	B/G	H_v	Θ_D	v_l	v_t	v_m	Refs.
SmB_2	138.7		126.8	291.5	0.15	1.09	27.6	577.9	6458	4145	4552	present
	148.7	145.24	122.42				17.98					(LSDA) Ref. [24]
	187.07	147.63	163.41				16.92					(LSDA + U) Ref. [24]
	128		110.8	258	0.16	1.16						(GGA)Ref. [28]
EuB_2	146.0		136.3	311.8	0.14	1.07	29.7	594.5	6582	4244	4659	present
	148.7	145.24	122.42				17.98					(LSDA) Ref. [24]
	132.82	131.03	89.935				17.4					(LSDA + U) Ref. [24]
	137.4		119.7	278.3	0.16	1.15						(GGA)Ref. [28]
GdB_2	151.4		143.4	326.9	0.14	1.06	31.3	598.9	6579	4256	4670	present
	170.36	162.85	126.86				17.56					(LSDA) Ref. [24]
	165.45	166.57	141.07				17.50					(LSDA + U) Ref. [24]
	131.2		113.5	264.3	0.16	1.16						(GGA)Ref. [28]
TbB_2	160		151.3	345.1	0.14	1.06	32.3	610.9	6679	4320	4740	present
	176.7	171.38	150.2				19.10					(LSDA) Ref. [24]
	159.67	170.87	142.79				18.77					(LSDA + U) Ref. [24]
	131.3		115.4	267.8	0.16	1.14						(GGA)Ref. [28]
DyB_2	167.4		158.4	361.2	0.14	1.06	33.3	617.4	6715	4344	4766	present
	160.38	171.12	151.08				19.34					(LSDA) Ref. [24]
	188.01	170.85	168.64				18.79					(LSDA + U) Ref. [24]
HoB_2	170.4		163.6	371.8	0.14	1.04	34.6	621.5	6706	4352	4773	present
	164.56	165.06	161.97				19.37					(LSDA) Ref. [24]
	184.7	169.88	155.49				18.50					(LSDA + U) Ref. [24]
ErB_2	172.9		168.2	381	0.13	1.03	35.8	624.5	6687	4352	4772	present
	169.47	168.8	148.64				19.59					(LSDA) Ref. [24]
	164.16	179.08	164.67				19.07					(LSDA + U) Ref. [24]
TmB_2	175.9		173	390.8	0.13	1.02	37	628.7	6682	4359	4778	present
	168.29	168.38	143.86				19.68					(LSDA) Ref. [24]
	150.57	149.14	189.4				19.56					(LSDA + U) Ref. [24]
	137.5		120.5	279.8	0.16	1.14						(GGA)Ref. [28]
LuB_2	180.7[a]		179.7[a]	404.8[a]	0.13[a]	1.01[a]	38.4	627.9[a]	6601.2[a]	4316.4[a]	4730.2[a]	(GGA)Ref. [21]
	204.35	200.52	183.51				20.31					(LDA) Ref. [24]
	178.4		173.3	392.7	0.13	1.03						(GGA)Ref. [28]

Table 6. The calculated isotropic bulk modulus (B in unit GPa), shear modulus (G in unit GPa), Young's modulus (E in unit GPa), Poisson's ratio (ν), hardness (H in unit GPa), Debye temperature (Θ_D in unit K), and sound velocity (v_l, v_t, and v_m, in unit m/s) for ReB_2 and OsB_2 structures.

Structure	Material	B	G	E	ν	B/G	H_v	Θ_D	v_l	v_t	v_m
ReB_2	SmB_2	67.6	31.4	81.5	0.30	2.15	3.1	314.2	4777	2558	2857
	EuB_2	70.0	33.0	85.5	0.30	2.12	1.3	319.1	4791	2578	2878
	GdB_2	71.6	34.1	88.2	0.29	2.10	3.6	318.4	4734	2555	2852
	TbB_2	73.3	35.2	91	0.29	2.08	3.8	321.0	4731	2560	2857
	DyB_2	74.8	36	93	0.29	2.08	3.9	320.5	4693	2541	2836
	HoB_2	76.3	36.6	94.6	0.29	2.01	4	320.1	4666	2524	2817
	ErB_2	77.7	37.2	96.2	0.29	2.09	4	319.9	4641	2509	2800
	TmB_2	79.5	38.1	98.5	0.29	2.08	4.1	321.4	4635	2506	2796
	LuB_2[a]	82.2	39.5	102.1	0.29	2.08	4.3	320.6	4576	2477	2764
OsB_2	SmB_2	121.3	86.3	209.2	0.21	1.405	15.2	487.9	5950	3595	3974
	EuB_2	126.2	94.4	226.6	0.20	1.336	17.4	505.1	6036	3694	4078
	GdB_2	129.5	100.3	239.1	0.19	1.291	19	510.6	6013	3712	4094
	TbB_2	133.3	104.8	249.1	0.19	1.271	19.9	517.5	6032	3737	4121
	DyB_2	166.8	155.9	356.6	0.14	1.069	32.4	612.7	6680	4309	4730
	HoB_2	170.1	160.9	366.9	0.14	1.057	33.6	616.6	6673	4316	4736
	ErB_2	172.5	165.5	376.1	0.14	1.042	34.8	619.7	6654	4317	4735
	TmB_2	175.5	170.3	386	0.13	1.03	36	624.0	6650	4325	4743
	LuB_2	179.8	177.2	400.1	0.13	1.014	37.6	623.7	6570	4288	4700

[a] GGA taken from Ref. [21].

The value of Poisson's ratio is indicative of the degree of directionality of the covalent bonds. The value of Poisson's ratio is small ($\nu = 0.1$) for covalent materials, whereas for ionic materials a typical value of ν is 0.25.[39] The calculated Poisson's ratios are about 0.1∼0.2 for AlB_2- and OsB_2-type structures. Therefore, the covalent contribution to the interatomic bonding for AlB_2-type structures is dominant. For the ReB_2 structure, the calculated Poisson's ratios are about 0.30. Hence, we conclude that the ionic contribution to the interatomic bonding is dominant for this structure. The calculated Poisson's ratios in the AlB_2 structure are lower than those for ReB_2 and OsB_2-type structures. The smaller Poisson's ratio implies that AlB_2 structure for rare-earth diborides is relatively stable against shear. Poisson's ratio also provides more information about the characteristics of the bonding forces than any of the other elastic constants. For central-force solids the ratio's lower and upper limits are 0.25 and 0.5, respectively.[40] Our ν values for the ReB_2 structure are close to 0.3 indicating that the interatomic forces are predominantly central forces. Our obtained values are smaller than the lower limit 0.25 in AlB_2 and OsB_2-type structures, which indicates that the interatomic forces are non-central in character. According to the criterion in Refs. [41] and [42] a material is brittle (ductility) if the B/G ratio is less than 1.75. The B/G ratios of AlB_2- and OsB_2-type structures are less than 1.75. Therefore, the compounds in AlB_2 and OsB_2 structures are classified as brittle.

Generally, hardness is related to the elastic and plastic properties of a material; and the shear modulus is a significantly better qualitative predictor of hardness than the bulk modulus. Besides the bulk and shear moduli, the elastic constant C_{44} is also an important parameter indirectly governing indentation hardness.[43] A number of semi-empirical models have been developed to predict the hardness of materials.[44–49] Recently, Chen *et al*.[48] proposed a new theoretical model to predict the hardness of polycrystalline materials based on the squared Pugh's modulus ratio ($k = G/B$) and the shear modulus (G) as follows:

$$H_v = 2\left(k^2 G\right)^{0.585} - 3. \quad (1)$$

This has been used successfully by Chen *et al.* to predict the hardness of a lot of compounds.[48]

We have used Eq. (1) to predict the Vickers hardness of the compounds under study and the obtained results are listed in Tables 5 and 6 for AlB_2-, ReB_2-, and OsB_2-type structures. Our results indicate that rare-earth diborides are hard materials in AlB_2 and OsB_2 structures, but they are soft in the ReB_2 structure. The present hardness values (see Table 5) are higher than those obtained in Ref. [24] for AlB_2 structure. We have to mention that the hardness of Gd–Lu diborides in AlB_2-type structure and Dy–Lu diborides in OsB_2-type structures are also very large ($H_v > 30$ GPa).

The bulk and shear moduli are still the most important parameters for characterizing hardness. In any instance of great hardness both moduli will be quite large.[50] As can be seen in Tables 5 and 6, both the AlB_2 and OsB_2 structures have larger bulk and shear moduli than the ReB_2 structure. The relative directionality of the bonding in the material also has an important effect on its hardness and is characterized by the value of G/B.[50,51] The calculated G/B for the Gd and Lu diborides in AlB_2-type structures and for the Dy and Lu diborides in OsB_2-type structures are larger than for the others under study, indicating more pronounced directional bonding between the ions.[50]

As is well known, the compounds of rare-earth metals with light sp elements (B, C, and N) possess strong covalent bonds, and their hardness is estimated numerically from *ab initio* calculations through the calculated elastic parameters (C_{ij}, B, G, and ν). In our case, the bond length d_{x-x} is relatively lower in the AlB_2 structure than in the ReB_2 or OsB_2 structure, and the calculated hardness value is higher in the former structure than in the others. These results imply that the value of H_v for a certain phase depends on its structure type, defining the character and forces of interatomic interactions in the studied compound, as observed recently in the OsB_2 polymorphs[52] and TcB_2 and ReB_2 compounds.[53] It is also known that the value of hardness is high in some covalent materials with shorter bond length, highly directional bonding, and higher density of valence electrons in covalent bonds.[54] These basic facts contribute to the differing hardness values for materials of the same or similar rare-earth diborides with different structures, doping types, and compositions (stoichiometries).

The Debye temperature is known to be an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature. At low temperatures the vibrational excitations arise solely from acoustic vibrations. Hence, at low temperatures the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. The Debye temperature and sound velocities calculated by using common relations given in Ref. [55]– [57] are listed in Tables 5 and 6 for structures under study. The TmB_2 compound in the AlB_2 structure possesses the largest Debye temperature (628.7 K), and this value is close to the Debye temperature of LuB_2 (627.9 K) in the same structure. The lowest Debye temperature (314.2 K) is found for SmB_2 in the ReB_2 structure.

4. Summary and conclusion

The calculated results presented for several ground states, structural, and mechanical properties for rare-earth diborides were investigated using first-principles calculations as implemented in VASP within the GGA approximation. The calcu-

lated structural parameters are in good agreement with previous results. The studied compounds are mechanically stable in all AlB_2-, ReB_2-, and OsB_2-type structures. The present results also show that EuB_2, GdB_2, TbB_2, ErB_2, and LuB_2 compounds energetically favor the AlB_2-type structure and do not exhibit any structural phase transition, but DyB_2, HoB_2, and TmB_2 undergo structural phase transitions at 39.8, 39.0, and 43.3 GPa, respectively. The SmB_2 compound can, again, easily transform from the OsB_2 to the AlB_2 structure under small pressure (1.47 GPa). Rare-earth diborides are hard materials in AlB_2 and OsB_2 structures, but they are soft in the ReB_2 structure. Consequently, we conclude that our theoretical predictions for the considered properties of rare-earth diborides would serve as a reliable reference for the future experimental and theoretical studies.

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