Prediction of new crystal structure phases in metal borides: a lithium monoboride analog to MgB$_2$.

Aleksey N. Kolmogorov and Stefano Curtarolo

Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708
(Dated: October 8, 2018)

Modern compound prediction methods can efficiently screen large numbers of crystal structure phases and direct the experimental search for new materials. One of the most challenging problems in alloy theory is the identification of stable phases with a never seen prototype; such predictions do not always follow rational strategies. While performing ab initio data mining of intermetallic compounds we made an unexpected discovery: even in such a well-studied class of systems as metal borides there are previously unknown layered phases comparable in energy to the existing ones.

With ab initio calculations we show that the new metal-sandwich (MS) lithium monoboride phases are marginally stable under ambient conditions but become favored over the known stoichiometric compounds under moderate pressures. The MS lithium monoboride exhibits electronic features similar to those in magnesium diboride and is expected to be a good superconductor.

FIG. 1: (color online). Known (AlB$_2$, V2) and proposed metal-sandwich (MS1, MS2) prototypes. The hexagonal layers of boron (grey) are separated by triangular layers of metal (yellow, only four atoms per layer are shown).
with *ab initio* calculations and found that MS1 and MS2 phases in one system, Li-B, are indeed stable enough to compete against known phases.

Present *ab initio* simulations have been performed with VASP \[14, 15\]; we use projector augmented waves (PAW) \[17\] and exchange-correlation functionals as parametrized by Perdew, Burke, and Ernzerhof (PBE) \[18\] for the Generalized Gradient Approximation (GGA). For comparison purposes we carry out tests in the Local Density Approximation (LDA) \[19\], and with ultrasoft (US) pseudopotentials \[20\]. We also employ an LAPW code WIEN2K \[21\] to plot characters of electronic bands and partial density of states (PDOS). All structures were fully relaxed. Numerical convergence to within about 2 meV/atom is insured by high energy cut-off (398 eV) and dense k-meshes \[22\].

Despite the potentially important application to batteries, the Li-B system is not fully explored and the question of the most stable monoboride phase remains open \[24, 25, 26, 27\]. Successful experimental attempts to synthesize lithium monoboride under ambient pressure date back to the 1970s \[28, 29\]. However, the structures were fully relaxed. Numerical convergence to within about 2 meV/atom is insured by high energy cut-off (398 eV) and dense k-meshes \[22\].

The relaxed cell parameters in the LAPW-GGA calculations are nearly the same as in the PAW-GGA \[14, 15\]. In this approach MS1-LiB is a little lower in energy (13 meV/atom below α-LiB) and the most stable of the three \[32\]. The PAW-LDA gives a much lower relative energy for MS1-LiB (42 meV/atom below α-LiB). A big discrepancy in the description of relative energies with the two approximations has also been seen in carbon systems with different types of bonding \[33\]; the GGA is expected to be more accurate. In all the tests above α-LiB and β-LiB remain 10 meV/atom apart. The independence of this result on the calculation approach can be explained by the similarities of the two structures, a trend also observed in other systems \[34\].

We conclude that within the accuracy of these calculations the MS1-LiB phase is comparable in energy to the known phases. Synthesis conditions could therefore be the deciding factor for which compound forms in the Li-B system at 50% concentration. We next evaluate the effect of hydrostatic pressure on the relative stability of the lithium monoboride phases. The three phases have very close volumes per atom at zero pressure. However, the α-LiB and β-LiB with linear boron chains are much harder than the sp$^2$-bound MS1-LiB: the respective volumes at P = 12 GPa are about 85%, 85%, and 69% of the zero-pressure values (interestingly, the intralayer bonds in MS1-LiB undergo non-monotonous expansion with pressure, stretching by about 2% at 5 GPa). The big compressibility of the MS1-LiB is an expected feature for a layered structure with a weak interlayer binding: at P = 12 GPa the c-axis shrinks down to 68% of its zero-pressure value, primarily due to the decrease in the Li-Li interplanar distance. The weakening of the metallic binding in the lithium bilayer is apparently caused by the significant charge transfer from lithium to the boron layer. The extreme softness of MS1-LiB suggests use of high pressures for synthesis of this phase. We plot the calculated enthalpies of the considered lithium monoboride phases with respect to α-LiB versus external pressure in Fig. 2. The plot shows that even if the MS-LiB are not the most stable phase at ambient pressure, they are quickly driven below the known phases and become favored by over 90 meV/atom at P = 12 GPa \[32\].

Note, that the hydrostatic pressure removes the degen-

![FIG. 2: (color online). Calculated relative enthalpy, ∆H(P)≡H(P)-H_{α-LiB}(P), as a function of pressure for lithium monoboride phases. The points are connected with splines. The larger yellow spheres are lithium atoms and the smaller black spheres connected with sticks are boron atoms.](image-url)
An important question is how to detect the new phases if they indeed form. Because the MS1 and MS2 are nearly degenerate at low pressures, the resulting structure at 50% concentration in Li-B could be a random mixture of the two and would be hard to detect with standard x-ray methods. Fortunately, the two phases have similar interlayer distances for boron and one would expect to see an x-ray peak (at interlayer distances for boron and one would expect to see an x-ray peak (at $\lambda = 1.5418\,\text{Å}$, zero pressure) in the range from $2\theta = 16.1^\circ$ for MS2 to $2\theta = 16.6^\circ$ for MS1. None of the observed peaks in the samples prepared at ambient pressure match these calculated values. Experimental effort to synthesize lithium monoboride at high pressures is highly desired.

Ab initio studies have shown that existence of energetically favorable phases could be barred by dynamical instabilities. We have investigated phonon modes at $\Gamma$-point with a force-constant matrix diagonalization method, implemented in VASP, using the MS2 structure with a convenient rhombohedral unit cell. MS2-LiB has two weakly interacting boron layers per unit cell which leads to an effective double-degeneracy of the known phonon modes at $\Gamma$ in the AlB$_2$-type compounds. Three of the remaining six optical modes, which involve sliding of undistorted layers, are rather soft. The soft modes are defined by the weakened interlayer Li-Li interaction and the perfectly stacked structure may actually be prone to small interlayer shifts, as there are two shallow minima at about 2% displacements of the in-plane lattice vector $a$ (see Fig. 3). We crudely estimate the frequency of the soft modes at $\Gamma$ by using all points up to 5% displacements and obtain $\omega_{x,y}=55\,\text{cm}^{-1}$ and $\omega_z=86\,\text{cm}^{-1}$. The modes at the A point are slightly softer ($\omega_{x,y}=37\,\text{cm}^{-1}$ and $\omega_z=59\,\text{cm}^{-1}$) but they remain real (interestingly, the frequencies are comparable to those in another layered structure, graphite). The interlayer sliding phonon modes along the $\Gamma$-$A$ direction are expected to be the softest optical phonon modes in the whole Brillouin zone: any finite $k_z$ would result in distortions of the rigid boron or lithium layers and a consequent phonon hardening. These considerations indicate that the MS2-LiB phase is dynamically stable. Hydrostatic pressure is again found to be a stabilizing factor: already at $P=2$ GPa the small distortions are suppressed and the frequencies of the softest x-y phonon modes are nearly doubled. Calculation of phonon modes for the full Brillouin zone is a subject of future study. With all the phonon branches calculated one can also estimate the vibrational entropy contribution to the Gibbs free energy to complete the analysis of the thermodynamic stability of MS-LiB.

The investigation of the phonon modes reveals that the actual stable unit of the MS-LiB phases is a hexagonal boron layer coated with two lithium layers on each side and can be related to graphene. Indeed, according to our estimates the cohesion per area between these B$_2$Li$_2$ sheets and their curvature energy are comparable to those for a carbon layer. One could speculate that if MS-LiB was exfoliated into such sheets, they might form carbon-like tubular or nanoporous structures. It would be interesting to see whether stable MS compounds could be obtained in other intermetallics based, for instance, on beryllium. Going beyond binaries also seems a promising direction to find more stable compounds: additional metal sites give more flexibility to experiment with different ternary alloys.

Finally, we give a brief discussion of the electronic properties of the MS phases focusing primarily on the $p$-states in boron, important for superconductivity in metal diborides. Our LAPW calculations show that the boron $p\sigma$ band along $\Gamma$-$A$ in MS2-LiB has practically no dispersion (Fig 3), an expected feature caused by the large separation between boron layers. Compared to a hypothetical AlB$_2$-LiB$_2$ phase the $\Gamma$-$A$ band downshifts by 0.6 eV and the $p\sigma$ PDOS at Fermi level drops by 25% to $N_{p\sigma}(0) = 0.046$ states/(eV-spin) per boron atom, which indicates higher filling of these bonding boron states. Note, that bonding $p\tau$ states also become occupied ($E_F$ is located exactly in the middle of the $p\tau$ pseudo-gap). The combination of these effects explains the dramatic stabilization of the lithium monoboride. Remarkably, the $p\sigma$ PDOS in MS2-LiB stays about 12% higher than that in MgB$_2$.

We find the frequency of the anharmonic $E_{2g}$ mode at $\Gamma$-point (649 cm$^{-1}$) in MS2-LiB to be quite close to...
PDOS units are states/(eV·spin) of states (PDOS) in MS2-LiB, calculated in LAPW\cite{21, 38}.

FIG. 4: (color online). Band structure and partial density of states (PDOS) in MS2-LiB, calculated in LAPW\cite{21, 38}. PDOS units are states/(eV·spin) per boron atom. The thickness of band structure lines is proportional to boron \( p_{x,y} \) (red) and \( p_z \) (green) characters.

that (624 cm\(^{-1}\)) in MgB\(_2\)\cite{23}, which can be related in part to the almost perfect match of the covalent boron-boron bond lengths\cite{11}. The similarities of the boron layer properties in these borides appear to extend to the electron-phonon coupling as well: following procedure in Ref. \cite{12}, we estimate the deformation potential \( D \) for the \( E_{2g} \) mode to be 13 eV/Å in both phases. Unlike the two-band superconductor MgB\(_2\), MS2-LiB has negligible contribution from the boron \( pr \) states at \( E_F \). These simple arguments suggest that the superconducting \( T_c \) in the MS2-LiB would be at least comparable to that in MgB\(_2\).

In conclusion, this work demonstrates that our knowledge of binary alloys is still incomplete and the identification of yet unknown phases may require new prediction strategies. The rather accidental finding of the MS structures is shown to be marginally stable under ambient conditions particularly suitable for the Li-B system: lithium mono-borides and whether MgB\(_2\)

We thank F.H. Cocks, V. Crespi, P. Lammert, R. Margine, and J. Sofo for valuable discussions.

\[1\] G. Ceder \textit{et al.}, Nature (London) \textbf{392}, 694 (1998).

\[2\] D. de Fontaine, in \textit{Solid State Physics}, edited by H. Ehrenreich and D. Turnbull (Academic Press 1994), \textbf{47}, pp. 33-176.

\[3\] A. Franceschetti and A. Zunger, \textit{Nature} \textbf{402}, 60 (1999).

\[4\] G.H. Johannesson \textit{et al.}, \textit{Phys. Rev. Lett.} \textbf{88}, 255506 (2002).

\[5\] G.L.W. Hart \textit{et al.}, \textit{Nature Materials} \textbf{4}, 391 (2005).

\[6\] S. Curtarolo \textit{et al.}, \textit{Phys. Rev. Lett.} \textbf{91}, 135503 (2003).

\[7\] D. Morgan \textit{et al.}, \textit{Meas. Sci. Technol.} \textbf{16}, 296 (2005).

\[8\] S. Curtarolo \textit{et al.}, \textit{Calphad} \textbf{29}, 163-211 (2005).

\[9\] R. Magri \textit{et al.}, \textit{Phys. Rev. B} \textbf{42}, 11388 (1990).

\[10\] MS1: 4 atoms in the primitive unit cell, space group R3m (#166). \( a = b, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ \), Wyckoff positions: M (0,0,1/6 − \( z_M \)/6), B (0,0,1/3+δ). LiB: \( a = 3.058 \) Å, \( c = 16.06 \) Å, \( z_M = 0.485, |\delta| < 10^{-3} \).

\[11\] MS2: 8 atoms, space group P63/mmc (#194). \( a = b, \alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ \), Wyckoff positions: M (4f) (1/3,2/3,1/4 − \( z_M \)/4), B1 (2b) (0,0,1/4), B2 (2d) (1/3,2/3,3/4). \( a = 3.057 \) Å, \( c = 11.04 \) Å, \( z_M = 0.496 \).

\[12\] J. Nagamatsu \textit{et al.}, Nature \textbf{410}, 63 (2001).

\[13\] J. Cortus \textit{et al.}, \textit{Phys. Rev. Lett.} \textbf{86}, 4656 (2001).

\[14\] T. Oguchi, J. Phys. Soc. Jpn. \textbf{71}, 1405 (2002).

\[15\] G. Kresse and J. Hafner, \textit{Phys. Rev. B} \textbf{47}, 558 (1993).

\[16\] G. Kresse and J. Furthmuller, \textit{Phys. Rev. B} \textbf{54}, 11169 (1996).

\[17\] P. E. Blochl, \textit{Phys. Rev. B} \textbf{50}, 17953 (1994).

\[18\] J.P. Perdew \textit{et al.}, \textit{Phys. Rev. Lett.} \textbf{77} 3865 (1996).

\[19\] D.M. Ceperley and B.J. Alder, \textit{Phys. Rev. Lett.} \textbf{45}, 566 (1980); J.P. Perdew and A. Zunger, \textit{Phys. Rev. B} \textbf{23}, 5048 (1981).

\[20\] D. Vanderbilt, \textit{Phys. Rev. B} \textbf{41}, R7892 (1990).

\[21\] An augmented plane wave+local orbitals program for calculating crystal potentials P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2K, Karlheinz Schwarz, Technical Universitat Wien, Austria, 2001.

\[22\] We use 20\( \times \)20\( \times \)23 for \( \alpha\)-LiB and \( \beta\)-LiB and 24\( \times \)24\( \times \)12 for MS1-LiB (with \( \Gamma \)-point included) meshes\cite{22}. Quadrupling the total number of \( k\)-points changes the relative energies by less than 1 meV/atom.

\[23\] J.D. Pack and H.J. Monkhorst, \textit{Phys. Rev. B} \textbf{13}, 5188 (1976); \textbf{16}, 1748 (1977).

\[24\] P. Villars, K. Cenzual, J. L. C. Daams, F. Hulliger, T. B. Massalski, H. Okamoto, K. Osaki, A. Prince, and S. Iwata, \textit{Crystal Impact, Pauling File, Inorganic Materials Database and Design System}, Binaries Edition, ASM International, Metal Park, OH (2003).

\[25\] Z. Liu \textit{et al.}, J. Alloys Compd. \textbf{311}, 256 (2000).

\[26\] H. Rosner and W.E. Pickett, \textit{Phys. Rev. B} \textbf{67}, 054104 (2003).

\[27\] H.B. Borgstedt and C. Gun院士, J. Phase Equilibria \textbf{24}, 572 (2003).

\[28\] F.E. Wang \textit{et al.}, J. Less-Common Met. \textbf{61}, 237 (1978).

\[29\] F.E. Wang, Metall. Trans. A \textbf{10}, 343 (1979).

\[30\] M. Worle and R. Nesper, Angew. Chem. Int. Ed. \textbf{39}, 2349 (2000).

\[31\] Due to the ionization of lithium atoms in Li-B compounds the \( 1s \) semi-core states in Li are likely to relax. Thus, in all PAW calculations we use the potentials where the \( 1s \) semi-core states are treated as core.
the MS1-LiB is 12 meV/atom below $\alpha$-LiB.

We use $R_{MT}^B = 1.35$ a.u., $R_{MT}^{Li} = 1.8$ a.u., $R_{MT} \cdot K_{max} = 8.0$, $l_{max} = 10$ and require the charge convergence to within $10^{-4}$. Since boron-boron bond lengths in the linear chains and in the hexagonal layers are quite different (by about 13%) we also check the dependence of the results on the muffin-tin radii used. Increasing $R_{MT}^B$ to 1.45 a.u. in $\alpha$-LiB, $R_{MT}^B$ to 1.6 a.u. in MS1-LiB and $R_{MT}^{Li}$ to 2.0 a.u. in both (the MT spheres do not overlap) changes the relative energies by less than 2 meV/atom. LAPW and APW+lo\cite{31} basis sets produce nearly identical results.

The formation enthalpy with respect to $\alpha$-B\cite{34} and fcc-Li becomes even more negative in the considered range of pressures. The known boron-rich compounds LiB\textsubscript{3} and Li\textsubscript{3}B\textsubscript{14}\cite{35,36} have large unit cells with fractional occupancies and cannot be presently evaluated with desired degree of accuracy.

We reproduce the 601 cm$^{-1}$ anharmonic frequency for MgB\textsubscript{2} obtained in US pseudopotential calculations\cite{37}. With the same simulation settings but in the PAW approach the frequencies are 23 cm$^{-1}$ higher. We expect the difference of the frequencies in MgB\textsubscript{2} and MS-LiB to be more accurate than the absolute values, which might not be properly evaluated in the frozen-phonon approach\cite{38}.

K. Kunc et al., J. Phys.: Condens. Matt. 13, 9945-9962 (2001).

M. Lazzeri et al., Phys. Rev. B 68, 220509 (2003).

J.M. An and W.E. Pickett, Phys. Rev. Lett. 86, 4366 (2001).

H. Rosner et al., Phys. Rev. Lett. 88, 127001 (2002).

A.M. Fogg et al., Chemical Communications 12, 1348 (2003).

R.J. Cava et al., Physica C 385, 8 (2003).

P. Zhang et al., Phys. Rev. Lett. 94, 225502 (2005).