Possible routes for synthesis of new boron-rich Fe-B and Fe_{1-x}Cr_{x}B_{4} compounds

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We use ab initio calculations to examine thermodynamic factors that could promote the formation of recently proposed unique oP10-FeB_{4} and oP12-FeB_{2} compounds. We demonstrate that these compact boron-rich phases are stabilized further under pressure. We also show that chromium tetraboride is more stable in the new oP10 rather than the reported oI10 structure which opens up the possibility of realizing an oP10-(Fe_{x}Cr_{1-x})B_{4} pseudobinary material. In addition to exhibiting remarkable electronic features, oP10-FeB_{4} and oP12-FeB_{2} are expected to be harder than the known Fe-B compounds commonly used for hard coating applications.

The renewed interest in transition metal (TM) borides stems, in part, from the materials’ potential to serve as hard, wear-resistant, chemically inert coatings. Combination of the TM and boron ensures a high valence electron density and a pronounced covalent bonding resulting in the compounds’ exceptional hardness; for example, ReB_{2} has been recently demonstrated to be the first metal-based bulk material that can scratch diamond. Metallicity and covalency are also key ingredients for phonon-mediated superconductivity and TM borides have received a lot of attention following the discovery of a remarkable MgB_{2} superconductor.

Iron borides have two particularly important industrial applications. First, homogeneously dispersed second-phase particles of Fe_{2}B are known to improve the tensile strength of low-carbon steels while pseudobinary Fe_{3}(B,C) and Fe_{23}(B,C) precipitates harden high-carbon steels. Second, Fe-B-based hard protective coatings are produced directly on the surface of steel via the process of boriding. During this thermochemical process boron diffuses into the steel forming either a single-phase (Fe_{2}B) or a duplex-phase (Fe_{2}B+FeB) coating layer. The two FeB and Fe_{2}B compounds have been shown to crystallize in the oP8 (or the related oS8) and tI12 configurations, respectively, and are the only low-temperature ground states listed in the latest experimental phase diagram. Synthesis of new boron-rich Fe-B compounds could have technological implications as the hardness of metal borides tends to increase with boron content. So far, except for the observation of a metastable FeB_{49} intercalation compound only two studies reported on the synthesis of amorphous and the AlB_{2}-type iron diboride but these compounds have not been reproduced.

Application of advanced compound prediction methods has recently allowed us to identify oP12-FeB_{2} and oP10-FeB_{4} candidate ground states with unique crystalline structures (Fig. 1a) that are stable relative to the known compounds. oP12-FeB_{2} was predicted to be the first metal diboride semiconductor while oP10-FeB_{4} was shown to have the necessary features to exhibit phonon-mediated superconductivity with a T_{c} of 15-20 K. The aim of this study is to examine synthesis routes that could lead to the discovery of the new materials. We find that both compounds are stabilized further under pressure while the oP10 Fe-based phase could be realized in the (Fe_{x}Cr_{1-x})B_{4} pseudobinary form. We also observe that calculated elastic constants of the predicted Fe-B compounds are higher than those in the known FeB and Fe_{2}B materials.

We use the projector augmented wave method as implemented in VASP and carry out full structural and spin relaxation for all compounds; relevant MB_{2} and MB_{3} metal borides show no magnetic ordering and their phonon and electron-phonon (ε-ph) properties are examined without spin polarization. The chosen energy cutoff of 500 eV and dense Monkhorst-Pack k-meshes ensure numerical convergence of formation energy differences to typically 1-2 meV/atom. We employ the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (xc) functional within the generalized gradient approximation (GGA). Vibrational corrections to Gibbs energy are calculated with PHON. The strength of the ε-ph coupling for oP10-CrB_{4} is evaluated within the linear response theory using the Quantum-ESPRESSO package. The boron ground state is simulated as α-B, known to be stable at medium pressures up to ~ 19 GPa. The iron ground state is taken as bcc and hcp at 0 and 20 GPa, respectively.

The peculiar oI10-TMB_{4} phases comprised of tetragonal B nets (Fig. 1a) were previously examined within the extended Hückel method; it was concluded that maximum binding in the 3d series is achieved for Cr and that the electron-rich Fe, Co, and Ni tetraborides may be unstable in this configuration. Our calculations showed dynamical instability of the oI10-FeB_{4} phase which gains a considerable 0.13 eV/f.u. in enthalpy by transforming into the oP10 structure (Fig. 2b). In the present study we observe a similar behaviour in the Cr-B system: oI10-CrB_{4} is found to be both dynamically (Fig. 1a) and thermodynamically (by 0.03 eV/f.u.) unstable relative to oP10. Although the boron network undergoes a significant distortion in the oI10→oP10 transformation, the lattice parameters and the simulated powder diffraction patterns (Fig. 2 in Ref. [31]) remain close which may explain why the structure of CrB_{4} was originally solved as oI10. These findings suggest that Fe_{x}Cr_{1-x}B_{4} compositions may assume the oP10 structure as well un-
under standard synthesis conditions. Indeed, there were no special requirements regarding the heat treatment or the starting materials (apart from cold compacting of the MB powders) for the past synthesis of ternary Fe-Cr-B materials, e.g., the ordered metal-rich Mn4B-type alloy or the O8-FeB- and O8-CrB-type compounds with partial substitutions of the host metal.

The effect of the composition on the thermodynamic and electronic properties of the ordered O8-Fe2Cr1-xBx compounds is investigated via supercell simulations [32, 33] see Fig. 2. We observe a sizeable stabilization, up to 28 meV/f.u., of the O10 structure at x = 0.5, Fig. 2a. The configurational entropy contribution from the disorder in population of metal sites is comparable at elevated temperatures: \( \Delta G_{\text{conf}}(T) = -k_B T [x \ln x + (1-x) \ln (1-x)] \) would be 60 meV/f.u. at \( T = 1000 \text{ K} \) and \( x = 0.5 \) if all decorations were degenerate in energy. Hence, the resulting ordering of Fe and Cr on the metal sublattice will depend on the quenching conditions. The density of states (DOS) is found to be sensitive to initial composition and drops rapidly in going from pure FeB4 (1.0 states/(spin eV atom)) to pure CrB4 (0.18 states/(spin eV atom)), Fig. 2b. Our linear response theory calculations [26, 36] give a small c-ph coupling (\( \lambda \approx 0.15 \)) and a negligible critical temperature \( (T_c < 1 \text{ K}) \) in O10-CrB4 indicating that superconductivity in this pseudobinary will require high Fe concentrations.

Application of medium pressures (a few GPa) in multi-anvil or diamond anvil cell setups may promote the formation of the materials in the predicted configurations by improving the compounds’ thermodynamic stability or the reaction kinetics. Successful examples of this synthesis route include boron-rich CaB6 and NdB6 or metal-rich Fe3B materials [37, 38]. We have examined the response to the hydrostatic pressure of over 40 known and proposed ambient-pressure M-B structure types listed in Ref. 31 by calculating their formation enthalpies at \( P = 20 \text{ GPa} \). We find that O8-FeB is the lowest-enthalpy phase and that the necessary condition for a boron-rich phase to be thermodynamically stable is to lie below the O8-FeB+α-B tie-line. Due to the remarkable compactness (Fig. 1d) of the predicted O10-FeB4 and O12-FeB2 phases (a respective 5% and 7% reduction in atomic volume compared to mixture of α-B and FeB) pressure does lead to much lower relative formation enthalpies for both compounds (Fig. 1c). Above \( P = 10 \text{ GPa} \), O10-FeB4 becomes thermodynamically stable relative to α-B and O12-FeB2 at all temperatures (Fig. 1f).

The compactness of these Fe-B phases also opens the perspective of obtaining new metal-based hard materials. It has been argued that the extraordinary hardness

![FIG. 1](Image)

**FIG. 1:** (Color online) a–c) Boron-rich structures: iron and boron are shown as large cyan and small black spheres, respectively. d) Atomic volume as a function of pressure. e) Relative enthalpy of O12-FeB2 and O10-FeB4 candidate phases w.r.t. the α-B+O8-FeB tie-line. f) Relative Gibbs energy (with vibrational contributions included using PHON) of O10-FeB4 w.r.t. α-B+O12-FeB2 at 0 K with and without zero point energy (ZPE) and at 1000 K.

| \( \text{Fe}_2\text{B} \) | \( \text{FeB} \) | \( \text{FeB}_2 \) | \( \text{FeB}_4 \) | \( \text{ReB}_2 \) |
|---|---|---|---|---|
| \( t12 \) | \( \text{oP8} \) | \( \text{oI16} \) | \( \text{oP12} \) | \( \text{oP10} \) |
| \( B(\text{GPa}) \) | 228 | 287 | 257 | 286 | 311 | 274 | 339 |
| \( G(\text{GPa}) \) | 143 | 138 | 153 | 157 | 231 | 187 | 266 |
| \( E(\text{GPa}) \) | 355 | 358 | 383 | 399 | 556 | 457 | 632 |
| \( \nu \) | 0.24 | 0.29 | 0.25 | 0.27 | 0.20 | 0.22 | 0.19 |

**TABLE I:** Calculated bulk \( (B) \), shear \( (G) \), and Young \( (E) \) moduli and Poisson ratio \( (\nu) \) for known and predicted Fe-B phases. hP6-ReB2 is added for comparison.

![FIG. 2](Image)

**FIG. 2:** (Color online) a) Relative stability of the pseudobinary O10-FeB\(_{1-x}\)Cr\(_x\)B\(_4\) compound. b) Total and projected density of states (DOS) for lowest enthalpy compounds.
of the ReB$_2$ material arises from an efficient packing of B into hcp-Re that results in only a 5% expansion of the metal lattice and, consequently, in the shortest TM-TM distances for any TM diboride.$^2$ The importance of having strong TM-TM and TM-B bonds is that the (0001) plane in hP6-ReB$_2$ supports the weakest stress. In the predicted oP12-FeB$_2$, the TM-TM (TM-B) bonds are shorter by 11% (9%) not only because of the smaller size of Fe but also because of the break-up of the B layers into B chains which tilt to accommodate the metal atoms (Fig. 3 in Ref. 31). This leads to a more pronounced relative deviation from Vegard’s law$^{10}$ in oP12-FeB$_2$ (-16.4%) compared to that in hP6-ReB$_2$ (-6.4%). A qualitative analysis of the materials hardness can be done by comparing shear moduli, as they have been shown to correlate with hardness in some cases.$^2$ The shear moduli in the predicted B-rich phases are at least as high as in the known oP8-FeB and tll2-Fe$_2$B compounds (Table I). Although elastic constants alone are not sufficient for a quantitative prediction of materials hardness,$^{12}$ it is encouraging to find the elastic moduli and the Poisson ratio in oP12-FeB$_2$ to be comparable to those in hP6-ReB$_2$ (see Tables I and II in Ref. 31 for comparison of experimental and theoretical values).

In summary, our high-throughput simulations spanning a large library of known and proposed structures predict consistently that new compounds should form under accessible synthesis conditions in such a common binary system as Fe-B. Ground state search under ambient or elevated pressures can be expanded further by performing unrestricted structural optimization driven, e.g., by evolutionary algorithm$^{20}$ for larger unit cells and other Fe-B compositions. Due to the known exceptional complexity of metal boride structures,$^{13}$ experimental input may be key for determination of the true ground states.

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See supplementary material at [URL will be inserted by AIP] for additional explanations, figures and tables.

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Since \textit{W}\textsubscript{0.5}Os\textsubscript{0.5}B\textsubscript{2} is known to assume the ReB\textsubscript{2} prototype we also examined ordered Fe\textsubscript{0.5}Cr\textsubscript{0.5}B\textsubscript{4} in the related mS10-MnB\textsubscript{4} supercell configurations but found them to be less stable by 22 meV/f.u w.r.t. the CrB\textsubscript{4}-FeB\textsubscript{4} tie-line.

We employ ultrasoft pseudopotentials [D. Vanderbilt, Phys. Rev. B \textbf{41}, R7892 (1990)] with a cutoff of 43 and 344 Ry for the wave functions and charge density, respectively. A $6 \times 6 \times 12$ \textit{k}-point mesh with a Gaussian smearing of 0.02

Ry and a $3 \times 3 \times 6$ \textit{q}-mesh are used for phonon dispersion calculations; a $12 \times 12 \times 24$ \textit{k}-mesh is used to evaluate the e-ph coupling. Calculation of the electron-phonon coupling in oP10-FeB\textsubscript{4} with these settings gives $\lambda \approx 0.8$.

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Supplementary material to: Possible routes for synthesis of new boron-rich Fe-B and Fe$_{1-x}$Cr$_x$B$_4$ compounds

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![Diagram 1: Calculated formation enthalpy of Fe-B compounds at P = 20 GPa.](image1.png)

**FIG. 1:** (Color online) Calculated formation enthalpy of Fe-B compounds at $P = 20$ GPa. The cyan and red labels correspond to known and proposed ground states, respectively.

![Diagram 2: Comparison of competing P10- and CrB structures with relaxed lattice vectors of $a = 4.749$ Å, $b = 5.488$ Å, $c = 2.852$ Å and $a = 4.723$ Å, $b = 5.474$ Å, respectively: (a) simulated x-ray patterns for $\lambda = 1.5418$ Å; (b) calculated phonon dispersions showing dynamic instability of oP10-CrB$_4$ at $q = \Gamma$.](image2.png)

**FIG. 2:** (Color online) Comparison of competing oP10- and oP10-CrB$_4$ structures with relaxed lattice vectors of $a = 4.749$ Å, $b = 5.488$ Å, $c = 2.852$ Å and $a = 4.723$ Å, $b = 5.474$ Å, respectively: a) simulated x-ray patterns for $\lambda = 1.5418$ Å; b) calculated phonon dispersions showing dynamic instability of oP10-CrB$_4$ at $q = \Gamma$.

![Diagram 3: Nearest neighbor histograms in fully relaxed boron-rich Re-B and Fe-B structures. In oP10-FeB$_4$ the neighbors are shown only for one of the two 4g boron sites.](image3.png)

**FIG. 3:** (Color online) Nearest neighbor histograms in fully relaxed boron-rich Re-B and Fe-B structures. In oP10-FeB$_4$ the neighbors are shown only for one of the two 4g boron sites.

Library of structure types. We have considered over 40 commonly seen M-B and M-C structure types listed in the Inorganic Crystal Structure Database (ICSD). The list below is ordered by composition and specifies the Pearson symbol and the prototype for each entry.

1:12: cF52-UB$_{12}$; 1:7: oI64-MgB$_7$; 3:20: oS46-Na$_3$B$_{20}$; 1:6: cP7-CaB$_6$; 3:14: tI160-Li$_3$B$_{14}$; 1:4: tP20-UB$_4$, oI10-CrB$_4$, mS10-MnB$_4$, 1:3: tP20-LiB$_3$, hP16-Mo$_{0.8}$B$_3$; 2:5: hP21-Mo$_2$B$_{1.65}$; 1:2: hP3-ALB$_2$, oP6-RnB$_2$, hR18-MoB$_2$, oP12-PbCl$_2$, hP6-ReB$_2$, hP6-MoS$_2$; 2:3: oS20-V$_2$B$_3$, hP10-Ru$_3$B$_3$; 3:4: oI14-Ta$_3$B$_4$, 5:6: oS22-V$_5$B$_6$; 1:1: oP8-Fe$_x$B$_{1-x}$, oS8-Pr$_{0.67}$, tI16-Mo$_x$, oS-TiI, oP$_8$-TiSi, hP$_2$-WC; 5:4: hP18-Rh$_3$B$_4$; 11:8: oP38-Ru$_{11}$B$_8$; 3:2: tP10-U$_3$Si$_2$, aP30-Rh$_3$B$_{5.5}$; 5:3: tI32-Cr$_3$B$_4$; 2:1: tI12-CuAl$_2$; 7:3: hP20-Th$_7$F$_{33}$, oP40-Mn$_3$C$_3$; 5:2: mS28-Mn$_3$C$_2$; 3:1: oP16-Fe$_3$C, oS16-Re$_3$B$_5$, tI32-Ni$_3$P; 23:6: cF116-Cr$_{23}$C$_6$; 4:1: tP10-Be$_4$B. The structures proposed in our previous study include 1:4: oP10-FeB$_4$, 1:3: mP8-FeB$_3$, 1:2: oP12-FeB$_2$.

Comparison to published data. We use available information on stable iron and rhenium borides at ambient pressure to benchmark the performance of the generalized gradient approximation employed in this study. For tI12-Fe$_2$B and oP8-FeB our calculated magnetic moments, 1.85 and 1.16 $\mu_B$/Fe, are in good agreement with previously measured values of 1.91 and 1.03 $\mu_B$/Fe, respectively. As shown in Table II for tI12-Fe$_2$B the calculated heats of formation are close to the previously calculated values but are noticeably larger in magnitude compared to the measured ones; for oP8-FeB we observe
ΔH (kJ/mol of atoms) Ref.

|       |         |         |         |         |         |         |         |         |         |         |         |
|-------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| tI12-Fe₂B | exp.    | -22.30① | 5       |         |         |         |         |         |         |         |         |
|       | exp.    | -22.60② | 5       |         |         |         |         |         |         |         |         |
|       | exp.    | -23.71 ③ | 6       |         |         |         |         |         |         |         |         |
|       | exp.    | -(9.48-22.62) | 7   |         |         |         |         |         |         |         |         |
|       | theo.   | -32.09 ④ | 6       |         |         |         |         |         |         |         |         |
|       | theo.   | -29.67⑤ | 8       |         |         |         |         |         |         |         |         |
|       | theo.   | -30.30⑥ | 8       |         |         |         |         |         |         |         |         |

|       |         |         |         |         |         |         |         |         |         |         |         |
|-------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| oP8-FeB | exp.    | -35.60④ | 5       |         |         |         |         |         |         |         |         |
|       | exp.    | -32.30④ | 5       |         |         |         |         |         |         |         |         |
|       | theo.   | -35.48④ | 8       |         |         |         |         |         |         |         |         |
|       | theo.   | -36.08④ | 8       |         |         |         |         |         |         |         |         |

TABLE I: Heat of formation for two stable compounds in the Fe-B system (① reference states: α-Fe, β-B, T=298 K; ② reference states: γ-Fe, β-B, T=1385 K; ③ values originally given in eV/atom).

an excellent agreement between theory and experiment. The elastic constants are determined by fitting the total energy of distorted unit cells to polynomials of second-order in strain. In order to determine all independent elastic constants for a given cell type, the same number of different strains is used. For each applied strain in the range [−0.03 : 0.03] with 0.01 steps the internal coordinates were fully relaxed. We find a generally good agreement between the present and previously reported values for the elastic constants and moduli, see Table II.

TABLE II: Comparison of calculated elastic constants and moduli to previously reported theoretical and experimental values for selected known compounds. The elastic moduli were calculated using ① Voigt-Reuss-Hill theorem, ② equation of state, or ③ Voigt theorem.

|       | C_{11} | C_{12} | C_{13} | C_{22} | C_{23} | C_{33} | C_{44} | C_{55} | C_{66} | B   | G   | E   | ν   | Ref. |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|------|------|------|------|------|
| tI12-Fe₂B | theo.  | 389.8  | 169.6  | 218.5  | 282.2  | 114.0  | 89.2   | 249.7④| 60.2③ | 184.4 | 0.388| 9    |      | ⑦   |
|       | theo.  | 331.04⑤ | 152.77 | 397.22 | 0.3   | ⑥    |        |        |        |      |      |      |      |      |
|       | theo.  | 413    | 154    | 132    | 389   | 148   | 157    | 228   | 143    | 355  | 0.24 | This work |      |      |
|       | exp.   | 343    |        |        |        |        |        |        |        |      |      |      |      | 10   |
|       | exp.   | 290    |        |        |        |        |        |        |        |      | 11.12|      |      |      |
|       | exp.   | 300    |        |        |        |        |        |        |        |      |      |      |      | 13   |
|       | exp.   | 164    |        |        |        |        |        |        |        |      |      |      |      | 14   |
| oP8-FeB | theo.  | 371    | 250    | 188    | 431   | 209   | 505    | 207   | 118    | 194  | 287  | 138  | 0.29 | This work |      |
|       | exp.   | 284    |        |        |        |        |        |        |        |      |      |      |      | 10   |
|       | exp.   | 350    |        |        |        |        |        |        |        |      |      |      |      | 11   |
|       | exp.   | 600    |        |        |        |        |        |        |        |      |      |      |      | 13   |
|       | exp.   | 125-624|        |        |        |        |        |        |        |      |      |      |      | 15   |
| hP6-ReB₂ | theo.  | 641    | 159    | 128    | 1037  | 271   | 350③  | 283③ | 16     |      |      |      |      |      |
|       | theo.  | 631.3  | 158.4  | 133.8  | 1015.0| 257.0 | 347.7③| 273.5③| 17     |      |      |      |      |      |
|       | theo.  | 689    | 170    | 141    | 1090  | 281   | 369③  | 294③ | 696    | 0.19 | ⑧    |      |      |      |
|       | theo.  | 632    | 154    | 131    | 1005  | 248   | 339③  | 266③ | 632    | 0.19 | This work |      |      |
|       | exp.   | 360    |        |        |        |        |        |        |        |      |      |      |      | 19   |
|       | exp.   | 382    |        |        |        |        |        |        |        |      |      |      |      | 20   |
|       | exp.   | 371±22 | 302±18 | 712±43 |      |      |      |      |      |      |      |      |      | 21   |
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