High-Temperature Conventional Superconductivity in the Boron-Carbon system: Material Trends

Santanu Saha,1 Simone Di Cataldo,1,2 Maximilian Amsler,3,4 Wolfgang von der Linden,1 and Lilia Boeri2

1 Graz University of Technology, NAWI Graz, 8010 Graz, Austria
2 Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 5, I-00185 Roma, Italy
3 Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA
4 Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

(Dated: April 8, 2020)

In this work we probe the possibility of high-temperature conventional superconductivity in the boron-carbon system, using ab-initio screening. A database of 320 metastable structures with fixed composition (50%/50%) is generated with the Minima-Hopping method, and characterized with electronic and vibrational descriptors. Full electron-phonon calculations on sixteen representative structures allow to identify general trends in $T_c$ across and within the four families in the energy landscape, and to construct an approximate $T_c$ predictor, based on transparently interpretable and easily computable electronic and vibrational descriptors. Based on these, we estimate that around 10% of all metallic structures should exhibit $T_c$'s above 30 K. This work is a first step towards ab-initio design of new high-$T_c$ superconductors.

I. INTRODUCTION

For more than one century, the discovery of a room temperature superconductor has been considered one of the "holy grails" of condensed matter physics. Already at the end of the 60's, N.W. Ashcroft and V.Ginzburg predicted that under sufficiently high pressures hydrogen may be turned into an atomic metallic phase, which would behave as a high-temperature superconductor (HTS). However, until last year, the pressures involved in hydrogen metallization turned out to be prohibitive, even for the best high-pressure research labs worldwide.

In 2004, Ashcroft proposed that the metallization pressure may be sensibly reduced by exploiting chemical pre-compression of the hydrogen sublattice in H-rich compounds. SH$_2$, predicted in 2014 by Duan et. al, was experimentally found to be superconducting at 200 GPa with a $T_c=203$ K by the Eremets' group in 2015 in less than five years, the maximum $T_c$ in high-pressure hydrides was raised up to 265 K in LaH$_{10}$, predicted a few years before.

Although room-temperature superconductivity at high pressures is an impressive achievement by itself, practical applications of superconductivity require materials that can operate at ambient pressure. Thus, the main focus of superconductivity research is gradually shifting from room temperature superconductivity at high pressures to HTS at ambient pressure.

Proposals to realize HTS at ambient pressure based on the conventional electron-phonon ($ep$) mechanism - High-$T_c$ Conventional Superconductivity (HTCS) - date back to the early 2000’s, when the MgB$_2$ discovery showed that HTCS are best realized in covalent metals, where the high-phonon frequencies and strong $ep$ matrix elements typical of covalent bonds coexist with metallic behavior, which is a prerequisite for conventional superconductivity. Following this general principle, several hypothetical materials were proposed: notable examples are doped LiBC, hexagonal Li-B, graphene, etc. These are all chemical and structural analogs of MgB$_2$, proposed on the basis of simple physical arguments, but without a knowledge of the underlying thermodynamics.

Only recently, the wide-spread use of modern methods for crystal structure prediction (CSP) has permitted to address the crucial aspect of thermodynamics in material design. Combined with methods for high-throughput (HT) database screening and machine learning (ML), CSP methods are an unprecedentedly powerful tool driving a sudden acceleration in material discoveries in the last few years. However, compared to other problems of material research, their application to superconductivity is still at a very early stage due to two intrinsic problems: (i) for a large class of unconventional superconductors, including the high-$T_c$ cuprates, a quantitative theory of superconductivity is currently missing; (ii) for conventional superconductors where, on the other hand, $T_c$ can be predicted with remarkable accuracy, the cost of a single $T_c$ calculation is too high, to directly perform high-throughput screening of large databases of hypothetical materials.

This work is part of a larger project, in which we plan to investigate superconductivity trends across several families of conventional superconductors, to identify meaningful screening protocols to search for promising superconducting candidates. In this paper, we focus on boron-carbon (BC) structures, with a 50%-50% composition.

First, we generate a large database of 320 distinct metastable boron/carbon structures with the minima hopping method (MH). The whole set is then analyzed to identify the main structural templates characterizing the potential energy surface; on the basis of simple electronic and vibrational descriptors, the number of structures is progressively narrowed down to a set of sixteen representative structures, for which we perform...
full $T_c$ calculations, to identify and understand empirical trends governing superconductivity in BC systems.

The BC system is an ideal choice for a first blind study of superconductivity, because both boron and carbon are light elements which tend to form stiff, directional bonds, favorable for HCTS; furthermore, both elements exhibit a strong tendency to polymorphism, which ensures that the pool of structures generated by MH will be large and diverse. Several studies in literature have already predicted conventional superconductivity with sizable $T_c$ in the boron-carbon system for selected compositions and structural motifs; a series of pioneering works by Moussa and Cohen analyzed $T_c$ trends in selected templates, using the rigid-band approximation for doping and the rigid-muffin-tin approximation for the $cp$ coupling. But to our knowledge this is the first work which exploits CSP methods to generate physically-meaningful structures and systematically investigate their superconducting properties.

The boron-carbon phase diagram is extremely complex; hexagonal and tetrahedral motifs, characteristic of $C \ sp^2/\ sp^3$ bonds, dominate the energy landscape up to $\sim 1/3 : 2/3 \ C : \ B$ compositions, while more complex motifs develop for higher $B$ concentrations, due to an increasing role of electron-deficient boron. To limit the scope of our analysis, we decided to focus on the single 50%-50% composition, where the physics and chemistry should still be dominated by carbon, but boron is in a sufficiently high concentration to ensure that many phases will exhibit a pronounced metallic behavior.

This paper is organized as follows. In section II we discuss the general features of the whole pool of 320 structures, their classification into different families and their salient qualities. We also describe briefly how the sixteen representative structures are selected for our subsequent superconductivity studies. In section III we discuss the trends in $T_c$ amongst different structures, and how they are correlated with electronic structure quantities. In section IV we discuss in greater detail the electronic, vibrational and superconducting properties of the structures. In section V we show that a simple analytical expression interpolates the $T_c$ of the representative structures, and may be used as a predictor for superconductivity. Finally in section VI we summarize the main conclusions of our work. Appendix A contains plots of the electronic and phononic DOS, and Migdal-Eliashberg spectral functions for the sixteen representative structures, while the methodology used for this study is discussed in greater detail in the Appendix B. In addition convex hull has also been provided in Appendix B.

II. STRUCTURES : THERMODYNAMICS AND PROTOTYPES

All structures considered in this work have a 50%/50% B/C stoichiometry, and can be described with an 8-atoms unit cell ($B_4C_4$). This choice leaves out some interesting structural prototypes, such as nanotubes and fullerenes, but is a reasonable compromise between computational efficiency and structural flexibility.

Our initial MH runs produced around $\sim 630$ such structures. Through post-relaxation of this initial pool with tighter settings and removal of duplicates, we ended up with a final tally of 320 unique structures. The Energy vs Volume plot of these structures is shown in the upper panel of Fig. 1. The energy shown here is the formation energy, computed using the graphite structure for Carbon and $\alpha$-Rhombohedral-$B_{12}$ for Boron as references. All the BC structures are metastable with positive formation energies in the range 0.1-1.0 eV/atom. Although large, these values lie within the synthesizability threshold defined in Ref. [39] for carbon polymorphs. Also, note that the formation energy may be sensibly reduced by choosing a different initial carbon structure for the synthesis which is closer to the target candidate.

The colors and symbols in Fig. 1 indicate the different families each structure belongs to, i.e. blue triangles for graphite (G), inverted green triangles for slab (S), grey circles for diamond (D) and red circles for tubulane (T). The classification of the structures into different families was done by hand, based on the relative arrangement of tetrahedral/triangular motifs and on the fraction of $sp^3$, $sp^2$ and $sp^3$ bonds.

The combined variation of bonding fraction and the spatial arrangement of the tetrahedra and triangles formed by $sp^3$ or $sp^2$ bonds makes some of the BC structures different from diamond or graphite. Their motifs are similar to those which have already been reported in pure carbon structures, and classified as "interpenetrating graphene networks" (IGN) or "carbon honeycombs" (CHC). We have grouped these structures under the general keywords tubulanes. In addition, we have created a new category slab, to accommodate structures whose representative motifs have not been reported in literature till date.

The characteristic features of the four different families are summarized below:

- **Diamond** [grey circles, Fig. 1(a)]
  Diamond structures are characterized by dominant $sp^3$ bonding, which makes them occupy small volumes. Indicated by grey circles, the diamond structures are situated on the left side in the Volume vs Energy plot in Fig. 1.

- **Graphite** [blue triangle, Fig. 1(b)]
  Graphite structures are characterized by atomically thin layers stacked on top of each other. The majority of atoms within one layer are bonded through $sp^2$ bonding. The layers interact weakly through van-der Waals interaction. This makes them occupy large atomic volumes as indicated by the location of the blue triangles in the right half of Fig. 1.

- **Slab** [inverted green triangles, Fig. 1(c)]
  A slab structure is geometrically similar to a
Figure 1. The Volumes vs Formation Energies of all predicted BC structures are shown in (Å³/atom) and (eV/atom) respectively. The formation energy is calculated w.r.t the energy of graphite and α-Rhombohedral-B₁₂. The colored symbols in the plot indicate the family of the structure, i.e. diamond (D) structures are represented by grey circles, graphite (G) by blue triangles, slab (S) by inverted green triangles and tubulane (T) by red circles. Large dark-coloured symbols indicate the sixteen representative structures which we selected for further study, while the rest are shown by small light-coloured symbols. Typical structures of the families diamond, graphite, slab and tubulane are shown in (a), (b), (c) and (d) respectively; black spheres represent atoms and off-white cylinders bonds. Considering the full convex hull, the formation enthalpy may be uniformly shifted up or down, depending on the carbon precursor.

The word *tubulane*, first reported by Baughman et. al. in 1993, refers to structures which display 3D networks of tubular structures. These tubes can be of any shape i.e. rhombohedral, hexagonal, circular etc. The structures of the family IGN and CHC mentioned above fall in this category. As a typical example, Fig.1(d) displays a tubulane with rhombohedral tubes. The constituent atoms in a tubulane can be connected via $sp^1$, $sp^2$, $sp^3$ bonds. With the possibility of having diverse mixture of bonds and tubes of different shapes, tubulanes can exhibit wide variability of atomic volumes, as shown by the wide distribution of the red circles in Fig.1.

Note that a proper estimate of the formation enthalpy
of BC structures should take into account not only the B and C end members, but also intermediate compositions. We thus evaluated the convex-hull of BC, including the B and C end members, but also intermediate compositions. We thus evaluated the convex-hull of BC, including the B and C end members, but also intermediate compositions. Taking the B\(_1\) phase into account,\(^ {32}\) the actual formation enthalpies are then 470 meV lower than in Fig. 1 – see Appendix B, Fig. 20. Many of the BC phases considered in this work may thus be synthesized, using the appropriate C precursor.

### III. SUPERCONDUCTING TRENDS OF REPRESENTATIVE STRUCTURES

Superconductivity calculations are around two orders of magnitude more expensive than the total energy and structural relaxation runs used to construct our initial database of structures. In order to narrow down our pool of potential superconductors, we first pruned out those structures, which have too high formation energies to be synthesizable, are dynamically unstable or exhibit poor metallic character and lack the stiff bonds, which are essential prerequisites for conventional HTS.

This was done by computing the value of electronic density of states (DOS) at the Fermi level \(N(E_F)\) and the vibrational frequencies at the zone center \(\omega_i\) for all structure in the database (DB). These quantities, together with the formation energy \(\Delta E\), were used to perform a preliminary screening, which left us with 116 potential candidates for HTS. As this number was still an order of magnitude too large to afford full \(T_c\) calculations, we manually hand-picked sixteen representative candidates for accurate superconductivity calculations, shown as dark colored symbols in Fig. 1 – see Appendix B, Fig. 20. Many of the BC phases considered in this work may thus be synthesized, using the appropriate C precursor.

| ID  | Space | Vol  | \(\Delta E\)  | \(N(E_F)\) | \(\omega_{\text{max}}\)  | \(\omega_{\text{avg}}\) | \(\lambda/N(E_F)\) | \(\omega_{\text{log}}\) | \(T_c\) | Bond Type |
|-----|-------|------|---------------|------------|-----------------|----------------|-----------------|----------------|--------|-----------|
|     | Gr. Ind. | (Å\(^3\)) | (meV) | (states/eV) | (meV) | (meV) | (K) |
| D01 | 164   | 6.30 | 170 | 0.15 | 160 | 79 | 0.6 | 4.2 | 72 | 21 | ✓ | X | ✓ | ✓ |
| D02 | 008   | 6.47 | 190 | 0.12 | 162 | 84 | 0.5 | 4.3 | 62 | 10 | ✓ | X | ✓ | ✓ |
| D03 | 051   | 6.46 | 270 | 0.16 | 152 | 92 | 0.8 | 4.9 | 72 | 35 | ✓ | ✓ | ✓ | ✓ |
| D04 | 160   | 6.92 | 420 | 0.21 | 128 | 92 | 0.8 | 3.9 | 52 | 30 | X | X | ✓ | ✓ |
| D05 | 216   | 6.56 | 440 | 0.36 | 106 | 71 | 2.3 | 6.3 | 41 | 75 | X | ✓ | ✓ | ✓ |
|     |       |       |     |       |     |     |     |     |     |     |     |     |     |     |     |
| Graphite | G01 | 012 | 8.57 | 360 | 0.09 | 186 | 95 | 0.4 | 4.1 | 42 | 2 | ✓ | ✓ | ✓ | ✓ |
| G02 | 012 | 8.63 | 360 | 0.11 | 186 | 95 | 0.4 | 3.4 | 39 | 1 | ✓ | ✓ | ✓ | ✓ |
| G03 | 002 | 8.91 | 390 | 0.08 | 198 | 104 | 0.4 | 4.3 | 32 | 1 | ✓ | ✓ | ✓ | ✓ |
| Slab | S01 | 164 | 6.96 | 190 | 0.16 | 161 | 76 | 0.6 | 4.1 | 79 | 25 | ✓ | X | ✓ | ✓ |
| S02 | 156 | 7.07 | 440 | 0.21 | 138 | 72 | 1.1 | 5.3 | 57 | 53 | ✓ | ✓ | ✓ | ✓ |
| Tubulane | T01 | 044 | 10.02 | 150 | 0.14 | 184 | 98 | 0.3 | 1.9 | 44 | 0 | ✓ | X | ✓ | ✓ |
| T02 | 071 | 7.47 | 180 | 0.14 | 156 | 95 | 0.6 | 3.9 | 42 | 9 | ✓ | ✓ | ✓ | ✓ |
| T03 | 012 | 7.12 | 260 | 0.25 | 163 | 88 | 0.7 | 2.8 | 58 | 24 | ✓ | ✓ | ✓ | ✓ |
| T04 | 044 | 6.83 | 310 | 0.16 | 149 | 90 | 0.6 | 3.9 | 51 | 15 | ✓ | ✓ | ✓ | ✓ |
| T05 | 001 | 6.85 | 360 | 0.21 | 149 | 85 | 1.2 | 5.4 | 37 | 37 | ✓ | ✓ | ✓ | ✓ |
| T06 | 006 | 7.00 | 380 | 0.22 | 138 | 84 | 0.9 | 4.1 | 60 | 42 | X | ✓ | ✓ | ✓ |

Table I. Summary of calculated properties of representative BC structures belonging to different families i.e. diamond (D), graphite (G), slab (S) and tubulane (T). The structures are represented with an id(first column), where the first letter represents the family and the last two integers, their energy ranking. The space group indexes of the structures are listed in the second column. The quantities volume (Å\(^3\)), energy(\(\Delta E\) in meV) and electronic density of state at the Fermi level \(N(E_F)\) are given per atom. For each family, the lowest-energy C structure and the e-\(\alpha\)-Rhombohedral-B12 are considered as references for computing the formation energy of the structures. Quantities \(\omega_{\text{max}}\) (maximum frequency at the \(\Gamma\)-point), \(\omega_{\text{avg}}\) (average of the optical vibrational frequencies at the \(\Gamma\)-point) calculated for a 8 atom unit cell and the logarithmic average phonon frequency \(\omega_{\text{log}}\) in meV. The \(\epsilon_p\) coupling constant \(\lambda\) is dimensionless and the \(\epsilon_p\) matrix element \(\lambda/N(E_F)\) in (states/eV/atom)\(^{-1}\). The superconducting critical temperature \(T_c\) in K has been estimated using the McMillan-Allen-Dynes formula \(\lambda/\mu^*\) with \(\mu^*\) = 0.10. The last three columns lists the presence (✓) or absence (X) of C-C, B-B and B-C bonds respectively.
gives a reasonable account; the explicit inclusion of van-der-Waals corrections in DFPT calculations of the \( ep \) interaction is not yet implemented in any publicly available code.

Grouped by family, the structures are shown in Figs. 2-4 and their properties are summarized in Table I. In the following, the structures are represented by an alphanumeric id of the form AXY, where the letter A represents the family (Diamond, Graphite, Tubulane, Slab) and XY the energetic ranking. The CIF files of the sixteen representative structures can be found in the supplementary material (SM).

The first column in Table I lists the id of the selected structures. General quantities describing the geometry are in the second (Space Group index), third (Volume per atom) and in the last three columns, which indicate the presence (\( \checkmark \)) or absence (\( \times \)) of bonds between C-C, B-B and B-C respectively. The formation energy (\( \Delta E \)) and the electronic DOS at the Fermi level \( N(E_F) \) are in the fourth and fifth column respectively. Note that, in contrast to Fig. 1, here the \( \Delta E \) in each family is reported considering as reference the lowest-energy C structure within that family. For the D and G families, diamond and graphite were considered. For the S family, diamond was considered. For the T family, the structure IGN-Z33 from Ref. 44 was considered, which is a member of the IGN family and the lowest energy (0.1 eV/atom w.r.t. graphite) structure in the tubulane family. This structure has symmetric rhombohedral tubes where the 4 sides are made of 3 C chains arranged in zig-zag (ZZ) fashion, hence the name "Z33".

Column six and seven list the (\( \omega_{\text{max}} \)) (meV) and the average (\( \omega_{\text{avg}} \)) (meV) \( \Gamma \)-point vibrational frequency, evaluated on a 8 atoms unit-cell for all structures. The quantities \( \Delta E \), \( N(E_F) \) and \( \omega_{\text{avg}} \) have been used for a pre-screening of structures as discussed in Appendix B.

Quantities associated with superconducting properties listed in Table I are the \( ep \) coupling constant \( \lambda \), the approximate effective \( ep \) matrix element \( \lambda/N(E_F) \), the logarithmic average phonon frequency \( \omega_{\text{log}} \) (meV) and the superconducting critical temperature \( T_c \) (K) estimated with the McMillan-Allen-Dynes formula:

\[
T_c = \frac{\omega_{\text{log}}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right],
\]

with a standard value \( \mu^* = 0.10 \) for the Coulomb pseudopotential.

### A. Structural Properties

The structures listed in Table I are shown in Figs. 2-4. All diamond structures, which consist of a mixture of \( sp^2 \) and \( sp^3 \) bonds, contain B-C bonds. Structures D01 and D02 also contain C-C bonds. The C-C bond is shared by two opposite-facing tetrahedra, while the other three bonds of the tetrahedron are B-C bonds. Structure D03 is the only structure in the D family which contains B-B bonds. The structure consists of zig-zag chains of C and B ordered in a particular fashion to form \( sp^3 \) bonds. Both D04 and D05 only involve B-C bonds. The major difference between the two is that the structure D04 encompasses a mixture of \( sp^2 \) and \( sp^3 \) bonds, whereas D05 only contains \( sp^3 \) bonds.

The layers of the graphitic structures G01 and G02 are the same, and the two structures only differ in the relative arrangement of the layers. Unlike the layers of pure C-graphite, which are flat, these layers have a staircase shape and consist of hexagons formed by C-C and B-C bonds. The B atoms which form the edge of the staircase have coordination number \( \sim 4-5 \), and hence form bonds which cannot be classified as purely \( sp^2 \) or \( sp^3 \). The structure G03 contains flat atomic layers like graphite, in which arm-chair chains of C atoms are connected to or-
In general, three observations are in place:

1. In all families except graphite, we found structures with rather high values of the DOS at the Fermi level $N(E_F)$, and moderate to high $T_c$'s. We also observe that these structures with higher DOS and $T_c$ tend to have quite high formation energies $\Delta E$, of the order of 200-400 meV, which is close to the synthetizability threshold.\textsuperscript{[33]} The structure with the highest $N(E_F)$ is D05, which is a diamond structure with only B-C bonds in a perfect tetrahedral geometry. Other structures with high $N(E_F)$ are D04, S02, T05 and T06, which all exhibit $T_c$’s exceeding 30 K. All graphitic structures obtained from MH runs have rather small values of $N(E_F)$, and negligible $T_c$’s. We thus tried to construct graphitic structures with high $N(E_F)$ manually, through different homogeneous replacements of B in C graphite in a 8-atoms cell. However, we found that any arrangement of B atoms in C graphite induces buckling, and that these buckled structures are either dynamically stable non-metals or dynamically unstable metals. This observation confirms what has been observed in studies of B/N doping of single graphene sheets by Zhou et. al. and Mann et. al.\textsuperscript{[34]}

2. A second quantity exhibiting a remarkable correlation with the $T_c$ is the value of the highest vibrational frequency at the $\Gamma$-point ($\omega_{\text{max}}$) and, in particular, its reduction (softening) with respect to the same quantity in a reference structure of pure carbon. In general, the softening is more pronounced for structures with higher $N(E_F)$ and $\lambda$. Almost all diamond structures exhibit a remarkable softening of the highest vibrational frequencies ($\omega_{\text{max}}$), with respect to that of pure diamond ($164 \text{ meV}$). The softening is the highest for D05, where $\omega_{\text{max}}$ is reduced by a factor 0.65 compared to the reference value. On the contrary, graphite structures exhibit only a small softening, as compared to the the reference value for C graphite (195 meV). Tubulane structures also exhibit a strong softening of $\omega_{\text{max}}$, compared to the reference tubulane structure (ING-Z33 200 meV). It is hard to give a quantitative estimate of this effect for slab structures, because no dynamically-stable reference structure exists, but the reference value should lie somewhere between $sp^2$ diamond and $sp^2$ graphite, and both S01 and S02 exhibit a remarkable softening with respect to this value.

3. A third, more general correlation can be found across the whole database between $T_c$ and the types of bonds (B-B, B-C or C-C) present. In particular, structures which contain B-C bonds only have the highest $T_c$ within each family. Structures with/without C-C and B-B bonds along-with B-C bonds may or may not be superconductors. A close look at Figs.\textsuperscript{[2] [4] [5]} show that in structures containing B-B bonds, the B atoms are not part of $sp^2 \text{−} sp^3$.

---

**Figure 4. Representative BC crystal structures in the tubulane family. The B atoms are shown as blue spheres, C atoms as orange spheres and bonds in grey. The structures are marked by their id.**
bonds, but form multiple bonds. This leads to a sizable deformation of the structure, which reduces the symmetry, and causes a sensible reduction of \( N(E_F) \), and hence \( T_c \). For example, B atoms in G01, G02 and G03 form 4-5 bonds with both B and C. On the other hand, the role of C-C bonds in determining \( T_c \) is much less clear. Finally, it is interesting to note that, though both D04 and D05 only contain B-C bonds, they have different \( T_c \)’s. This difference can be associated to the fact that D05 only contains \( sp^3 \) bonds, whereas D04 contains a mixture of \( sp^2-sp^3 \) bonds, and also in this case the symmetry lowering leads to a \( T_c \) suppression.

### IV. ELECTRONIC STRUCTURE:

In this section, we present a detailed comparison of the electronic structure of the representative structures, to gain a microscopic insight of their superconducting properties, discussed only in general terms so far.

The electronic DOS’s, Phonon and electron-phonon spectra (Eliashberg functions) for our sixteen representative structures, divided by families, are reported in Appendix B, Figs. 8-19 in the electronic (Figs. 8-11) and phonon (Figs. 12-15) DOS plots, we report in red and blue the partial carbon and boron contributions as well as the total DOS in black. The top panels of all figures show reference spectra, calculated for a pure carbon structure.

The electronic DOS plots show an almost perfect hybridization between B and C states in all structures, with the two partial DOS’s closely following each other. In addition, the variation of the spectral distribution of the electronic states in different BC structures, compared to the reference pure carbon structures, is a good indicator of the changes in electronic structure due to rearrangement of bonds. In this respect, it is quite interesting to compare the behavior of structures in the diamond and graphite families, where it is straightforward to define a reference template for the pure structure. In both cases, in a simple rigid-band (RB) model the Fermi level, shown by the dashed line in the upper panels of Figs. 8-19, would fall into a \( \sigma \) (2D or 3D) band. In this case, one would predict a sizable \( ep \) coupling, as \( \sigma \) bonds are extremely stiff and sensitive to lattice distortions.

However, in most real structures, a substantial rearrangement of bonds and electronic states invalidates this simple line of reasoning, based on the RB approximation. In the diamond family, a substantial shift of spectral weight away from the Fermi level occurs, which is more pronounced for low-energy structures, where it produces a substantial lowering of the DOS at the Fermi; the shift is absent in D05, which can almost perfectly be described by the RB approximation. In the graphite family, all structures generated for 50% BC composition are either dynamically unstable, or weakly metallic, due to a major rearrangement of bonds. G01, G02 and G03 all contain B-B and C-C dimers, and/or buckled planes, and exhibit an extremely small \( N(E_F) \).

For slabs and tubulanes, due to the large variety of moieties and motifs, it is less straightforward to define a reference structure. We chose T06 and S02 as structural templates for the C reference structure for tubulane and slab respectively. Also in these cases, a pronounced shift of spectral weight away from the Fermi level is observed, which is reduced for higher-energy structures. The DOS of low-energy tubulanes, which are more open, resemble quite closely those of graphite structures, while high-energy ones tend to mimic those of diamond. The same tendency can be observed in slab structures.

Phonon DOS’s are shown in Figs. 12-15, again with the same color-code and definition of reference structures. As observed for electronic DOS’s, due to the similar B and C mass, the spectra have in general a fairly mixed character. However, the phonon DOS’s of structures which contain B-B or C-C bonds tend to exhibit sharp peaks of pure B- or C-character, corresponding to localized vibrations. Many of these peaks are found at high energies. In addition, a progressive reduction of the highest phonon frequency with increasing formation energy is also evident in all families. The effect is particularly spectacular in D05, where the reduction of the highest frequency is \( \sim 35\% \).

Figs. 16-19 show for each family the Migdal-Eliashberg(\( ME \)) \( ep \) constant \( \lambda(\omega) \) and report the average phonon frequency \( \omega_{\text{log}} \), given by:

\[
\lambda(\omega) = 2 \int_{0}^{\infty} \frac{\alpha^2 F(\omega')}{\omega'} d\omega'
\]

\[
\omega_{\text{log}} = \exp \left[ \frac{2}{\lambda} \int_{0}^{\infty} \alpha^2 F(\omega) \frac{\ln(\omega)}{\omega} d\omega \right]
\]

where \( N(E_F) \) is the electronic DOS at the Fermi level, and the two \( \delta \) functions restrict the sum to electronic states at the Fermi level with momenta \( \mathbf{k} \) and \( \mathbf{k}+\mathbf{q} \). The \( \omega_{\mathbf{q},\nu} \) is the vibrational frequency of mode \( \nu \) and wavevector \( \mathbf{q} \) and \( g_{\mathbf{k},\mathbf{k}+\mathbf{q},\nu} \) is the corresponding electron-phonon matrix element. On the same plots, with orange dashed-lines we show the frequency-dependent \( ep \) constant \( \lambda(\omega) \) and \( \omega_{\text{log}} \).
constant $\lambda$, obtained from Eq. \ref{eq:lambda} with $\omega = \infty$, tend to be larger for higher-energy structures, and range from 0.4 in graphite structures G01, G02 and G03 to 2.3 in diamond D05.

The main factor behind the large variation in $\lambda$ amongst structures is the variation of the electronic DOS at the Fermi level $N(E_F)$. This can be appreciated recalling that $\lambda$ can be rewritten using the so-called Hopfield expression: \[\lambda = \frac{N(E_F)\lambda^2}{M\bar{\omega}^2}, \tag{5}\]

where $\lambda^2$ is the $ep$ coupling matrix element averaged over Fermi surface, $M$ is the average atomic mass and $\bar{\omega}^2$ is the square of an average vibrational frequency. As reported in Table \ref{table:structures}, $V = \frac{\lambda}{N(E_F)}$ is $\approx 4.0$ in most structures considered in this work. The only notable exception is the diamond structure D05, where this ratio is $50\%$ larger than in all other structures, reflecting a qualitative difference in bonding with respect to all other structures.

In summary, the analysis of the electronic structure shows that most structural templates exhibit a similar tendency to superconductivity: the $ep$ coupling is spread out over several phonon modes, and the value of the $ep$ coupling constant $\lambda$, and hence $T_c$, is mostly determined by the value of $N(E_F)$, since the ratio $V = \frac{\lambda}{N(E_F)}$, is essentially constant across and within families. In most low-energy structures $T_c$ is suppressed by the formation of B-B and C-C bonds, which shifts electronic spectral weight away from the Fermi level, lowering the band energy, but also $N(E_F)$.

The presence of B-B and C-C bonds is also visible in the phonon spectra, where it leads to the formation of sharp peaks at high energies.

The diamond structure D05, where, due to the alternating arrangement of B-C atoms, the original symmetry of pure diamond is retained, and electronic states at the Fermi level have a pure $\sigma$ ($sp^3$) character, is a clear outlier of the database. Here, the DOS follows a perfect rigid-band behavior compared to pure diamond, while the phonon spectrum is strongly renormalized, due to coupling between bond-stretching phonons and $\sigma$ states. As a result, $V = \frac{\lambda}{N(E_F)}$ is around $50\%$ larger than in all other representative structures, and the predicted superconducting $T_c$ is also exceptional ($79\;K$), in line with the highest values calculated in Ref.\cite{ref:superconductivity}

These observations imply that general arguments based on the rigid-band analysis of fixed structural templates must be taken with care in BC\cite{ref:structure} because structural distortions and bond rearrangements can have a dramatic effect on $T_c$.

V. A SIMPLIFIED EXPRESSION FOR $T_c$;

The values of $T_c$, $\lambda$ and $\omega_{\text{log}}$ for all sixteen representative structures, collected in Table \ref{table:structures}, were computed using the McMillan-Allen-Dynes formula, Eq. \ref{eq:mcMillan}, which requires a full calculation of the electron-phonon (Eliashberg) spectral function - Eq. \ref{eq:Eliashberg}.

For an $8$-atoms unit cell with no symmetry, a calculation of $\alpha^2 F(\omega)$ with a reasonably-dense sampling of reciprocal space for electronic and phononic momenta requires around 3000 CPU hours on a computer cluster. This type of calculations are clearly unfeasible for large-scale high-throughput material screening, which was our primary motivation to pre-select only a few representative structures from our initial pool.

With the $T_c$ data at hand, it is interesting to see whether any trends in $T_c$ could have been foreseen on the basis of the simple electronic structure quantities that
we had used to pre-screen our structural database, which require a much less intense computational effort.

The three upper panels of Fig. 5 show that $T_c$ exhibits an almost linear correlation with $N(E_F)$, and an inverse correlation with both $\omega_{\text{max}}$ and $\omega_{\text{avg}}$. Although the two vibrational descriptors are approximately equivalent, $\omega_{\text{max}}$ is monotonous, while $\omega_{\text{avg}}$ incorrectly classifies the two slab structures and a few diamond ones. The lower panel of Fig. 5 shows that the calculated $T_c$'s when plotted as a function of $\frac{N(E_F)}{\omega_{\text{max}}}$ closely follow a linear behavior:

$$T_c = 26.9 K st.^{-1} eV^2 \cdot \left[ \frac{N(E_F)}{\omega_{\text{max}}} - 0.3 \right] \quad (6)$$

Although extremely simple, this formula seems to interpolate nicely the $T_c$ from different templates, and has a transparent physical interpretation.

That $T_c$ should positively correlate with $N(E_F)$ can be easily understood from the Hopfield's expression for $\lambda$ - Eq. 5. On the other hand, the correlation of $T_c$ with $\omega_{\text{max}}$ is less straightforward to understand. One aspect is probably phonon softening: in an interacting system of phonons and electrons, the same coupling which leads to superconductivity also leads to the renormalization of phonon frequencies, with respect to a bare, non-interacting value. In a simple model where a single phonon mode with frequency $\omega$ couples to a single electronic band, $\omega$ is reduced with respect to its bare value $\Omega$ as: $\omega^2 = \Omega^2(1 - 2\lambda)$. However, while the model of a single phonon mode may be safely applied to hole-doped diamond and graphite, where superconductivity is dominated by the zone-center bond-stretching optical phonon and $\sigma$-holes its applicability to structures where the RB model does not hold due to major structural rearrangements, and the coupling is spread out over several phonon modes and electronic states, is questionable. It is in fact possible that $\omega_{\text{max}}$ accidentally encodes both the presence of high-energy B-B or C-C phonon modes, due to the formation of B-B and C-C bonds, which are disruptive for HTCS, and the actual phonon softening of a large part of the phonon spectrum in systems where the coupling is strong. More tests are needed to check the general validity of this trend, even for a relatively specialized case as BC. This goes well beyond the aim of the present paper.

However, we can use our simple predictor for $T_c$ to estimate the tendency of BC structures to HTCS across the whole energy landscape. In Fig. 6 the model $T_c$ from Eq. 6 as a function of $\frac{N(E_F)}{\omega_{\text{max}}}$ is shown in four different panels for all metallic structures in the original DB, grouped by family. Around 60% of the predicted $T_c$ lie in the 10-20 K range, 25% between 20 and 30 K, and ~10% are above 30 K. These high-$T_c$ structures belong mostly to the tubulane and diamond families, a few to the slab family, whereas all graphite structures are predicted to exhibit $T_c$'s below 20 K. Note that also in this plot the structure D05, i.e. the data point with the highest $T_c$ in Fig. 5, is a complete outlier, and most likely its $T_c$ of 79 K is an upper bound for the BC system at 50%-50% composition.

Eq. 6 can also be used to obtain an estimate of the formation energy required to obtain structures for a specific range of $T_c$. In Fig. 7 the predicted $T_c$ for all metallic BC structures is plotted as a function of formation energy; the meaning of colors and symbols is the same as
in Fig. 1. We observe that, in general, the lowest-energy structures have $T_c$'s below 20 K. A large cluster of structures is also found, with $\Delta E$ between 300 and 400 meV, and $T_c$'s exceeding 30 K.

VI. CONCLUSIONS:

In this work, we probed the possibility of realizing HTCS in the boron-carbon system, using an ab-initio screening approach. First, we generated a large (320) database of metastable BC structures, with 50%/50% boron/carbon composition and 8-atoms unit cells, and showed that these can be grouped into four main families of characteristic motifs for pure carbon: diamond, graphite, slab and tubulane. From a first high-throughput screening based on the values of the electronic DOS at the Fermi level, zone-center vibrational frequencies, and formation energies, we estimated that around half of the generated structures are promising HCTS. From these, we selected sixteen representative structures, spanning a variety of motifs and structural templates, for which we performed full electron-phonon calculations. We identified several general trends amongst them: (i) In all families, except graphite, we could find superconductors with $T_c$'s $\approx 40$ K, comparable to the best-known ambient-pressure superconductors; (ii) Within one family, the value of $T_c$ is essentially determined by $N(E_F)$; (iii) $T_c$ correlates inversely with the highest phonon frequey at the zone-center, $\omega_{\text{max}}$. (iv) A geometric analysis of the selected structures shows that the highest $T_c$'s within a given family is usually found in structures where the fraction of B-C bonds is dominant with respect to other types of bonds, and particularly if these have $sp^3$ character. Structures where bonds centered around B atoms are neither $sp^2$ nor $sp^3$ tend to exhibit a low $T_c$, because the clustering of atoms around B tends to reduce the symmetry, depress the value of $N(E_F)$, and hence $T_c$.

The empirical observations (i)-(iii) can be distilled into a single analytical formula for $T_c$, which can be used as a predictor for HTCS. On the basis of this formula, we estimate that around $\sim 10\%$ structures have $T_c$ larger than 30 K, which makes them interesting candidates for HTCS. Most of these structures have formation energies between 300 and 400 meV, and may be synthesized using an appropriate carbon precursor. The diamond structure D05, which only has B-C bonds in $sp^3$ tetrahedral arrangement, sets an upper limit for $T_c \sim 80$ K for the BC system at 50%-50% composition. Given that $T_c$ is so strongly dominated by $N(E_F)$, it is however conceivable that $T_c$ may be improved by doping. This work is a first step in the identification of HTCS at ambient pressure in light-element covalent metals using ab-initio screening techniques.

ACKNOWLEDGMENTS

S.Saha, S. di Cataldo and W. von der Linden acknowledge computational resources from the dCluster of the Graz University of Technology and the VSC3 of the Vienna University of Technology, and support through the FWF, Austrian Science Fund, Project P 30269- N36 (Superhydra). M. Amsler acknowledges support from the Swiss National Science Foundation (projects P300P2-158407, P300P2-174475, and P4P4P2-180669). L. Boeri acknowledges support from Fondo Ateneo Sapienza 2017-18 and computational Resources from CINECA, proj. Hi-TSEPH.
Appendix A: Electron-Phonon Spectra of the Sixteen Representative structures

1. Electronic Properties

Figure 8. The top panel shows the electronic DOS of the reference diamond structure and rest, the total DOS(black) and partial contribution of C(red) and B(blue) atoms in all the diamond structures.

Figure 9. The top panel shows the electronic DOS of the reference graphite structure and rest, the total DOS(black) and partial contribution of C(red) and B(blue) atoms in all the graphite structures.

Figure 10. The top panel shows the electronic DOS of the reference slab structure and rest, the total DOS(black) and partial contribution of C(red) and B(blue) atoms in all the slab structures.

Figure 11. The top panel shows the electronic DOS of the reference tubulane structure and rest, the total DOS(black) and partial contribution of C(red) and B(blue) atoms in all the tubulane structures.

2. Vibrational Properties

The total(black) and partial phonon DOS(C in red and B in blue) of all the structures arranged by family are shown in Fig. 12(D), Fig. 13(G), Fig. 14(S) and Fig. 15(T).
Figure 12. The top panel shows the phonon DOS $F(\omega)$ of the reference diamond structure and rest, the total DOS (black) and partial contribution of C(red) and B(blue) atoms in all the diamond structures.

Figure 13. The top panel shows the phonon DOS $F(\omega)$ of the reference graphite structure and rest, the total DOS (black) and partial contribution of C(red) and B(blue) atoms in all the graphite structures.

Figure 14. The top panel shows the phonon DOS $F(\omega)$ of the reference slab structure and rest, the total DOS (black) and partial contribution of C(red) and B(blue) atoms in all the slab structures.

Figure 15. The top panel shows the phonon DOS $F(\omega)$ of the reference tubulane structure and rest, the total DOS (black) and partial contribution of C(red) and B(blue) atoms in all the tubulane structures.
Figure 16. The Eliashberg spectral function $\alpha^2 F(\omega)$ and $ep$ coupling constant $\lambda(\omega)$ of the diamond structures. The $\alpha^2 F(\omega)$ and $\lambda(\omega)$ of D05 is scaled down by 0.5

Figure 17. The Eliashberg spectral function $\alpha^2 F(\omega)$ and $ep$ coupling constant $\lambda(\omega)$ of the graphite structures.

Figure 18. The Eliashberg spectral function $\alpha^2 F(\omega)$ and $ep$ coupling constant $\lambda(\omega)$ of the slab structures. The $\alpha^2 F(\omega)$ of S01 is scaled down by 0.5

Figure 19. The Eliashberg spectral function $\alpha^2 F(\omega)$ and $ep$ coupling constant $\lambda(\omega)$ of the tubulane structures. The $\lambda(\omega)$ of T05 is scaled down by 0.5. For T06, both the $\alpha^2 F(\omega)$ and $\lambda(\omega)$ are scaled down by factor of 0.5
3. Electron-Phonon Spectra

Appendix B: COMPUTATIONAL METHODS

1. Structure Prediction and DFT Calculations

The minima hopping (MH) method was used for an efficient scanning of the potential energy surface to find low-energy structures. The DFT calculations for total-energy and relaxations were carried out using the Vienna Ab-initio Simulation Package (VASP) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and 0.1 KBar on stress was set for the relaxation. The energy cutoff used for the post-relaxation calculation was 500 eV. For the relaxation and energy evaluation, the energy cutoff used for the post-relaxation calculation was 380 eV, which ensures an accuracy of \( \sim 10 \) meV/atom.

The post-relaxation, energy evaluation and calculation of the electronic DOS of all structures were performed using VASP with same set of PAW potentials and PBE functional as used in the MH runs, but including van-der-Waals D3 dispersion corrections with Becke-Jonson damping. A threshold of 1 meV/Å force of each atom and 0.1 KBar on stress was set for the relaxation. The energy cutoff used for the post-relaxation calculation was 500 eV. For the relaxation and energy evaluation, the reciprocal (k) space integration employed a uniform k-grid with a resolution of \( 2\pi \times 0.10 \) Å\(^{-1}\) centered at the \( \Gamma \)-point a gaussian smearing of width 0.10 eV. For an accurate evaluation of the electronic DOS we employed the improved Tetrahedron method, as implemented in VASP.

2. Phonon and Electron-Phonon Coupling Calculations

The phonon calculations at the \( \Gamma \)-point on the post-relaxed structures and the complete phonon calculations of phonon spectra and \( ep \) matrix elements were carried out within Density Functional Perturbation Theory (DFPT), as implemented in the plane-wave pseudopotential code Quantum Espresso. Atoms were described by Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials. For the initial phonon calculations at the \( \Gamma \)-point on the large database of structures, a PBE functional was used, whereas the remaining calculations were done with ONCV pseudopotential, which ensures more accurate relaxations for layered structures. The \( ep \) matrix calculations were carried out on regular \( \Gamma \)-centered Monkhorst-Pack grid of \( 8 \times 8 \times 8 \) grids for phonons (q) and \( 8 \times 8 \times 8 \) grids for electrons (k). The selected structures were re-relaxed to a threshold force of 0.1 meV/Å and stress of 0.1 KBar prior to phonon and \( ep \) calculation with the LDA functional. For these calculations, an energy cutoff of 80 Ry was used with a Gaussian smearing of 0.04 Ry for k-space integration. For all structures, we employed a 8-atoms supercell. In the case of the D05 structure, where symmetry allowed us to reduce the structure to two atoms/cell, a phonon grid of \( q = 8 \times 8 \times 8 \) mesh was used.

3. Screening Protocol and Structure Selection

In this work, we have developed a three-stage protocol to identify superconductivity candidates from an initial pool of 320 metastable MH structures. In the first step, we wanted to prune out structures which had no potential for superconductivity. We thus needed to identify structure which should be: (i) plausible to be realized in experimental conditions, (ii) metallic (iii) dynamically stable and (iv) exhibit stiff directional bonds, which ensure large phonon frequencies and \( ep \) matrix elements.

Each of the three qualitative features can be estimated by the energy of formation \( \Delta E \) (i), electronic DOS at the Fermi level \( N(E_F) \) (ii), and the phonon spectrum (iii), respectively. The energy of formation and the electronic DOS were already calculated for all the 320 structures after the post-relaxation step.

For the dynamical stability, a full calculation of the phonon spectrum is too expensive to be feasible, whereas calculating the phonon frequencies \( \omega_i \) only at the \( \Gamma \)-point is relatively inexpensive. Hence, we calculated the \( \omega_i \)'s only at the \( \Gamma \)-point. This approach is not sufficient to assess the dynamical stability of the structure but it allowed us to reduce the pool of candidates, removing structures with imaginary \( \omega_i \)'s.

From the \( \omega_i \)'s, we further constructed a single-number descriptor \( \omega_{avg} \), which is an average of all optical phonon frequencies at the \( \Gamma \)-point.

With these three quantities, i.e. \( \Delta E \), \( N(E_F) \) and \( \omega_{avg} \), in hand, we then developed and used the following three-steps screening process:

- **Step 1:** Structures with \( \Delta E \leq 0.5 \) eV/atom w.r.t Graphite and \( \alpha \)-Rhombohedral-B\(_{12}\) are retained.
- **Step 2:** Structures with \( N(E_F) \geq 0.1 \) states/eV/atom are retained.
- **Step 3:** Structures with \( N(E_F) \times \omega_{avg} \geq 0.02 \) states/atom are retained.

These requirements are still broad enough that the initial subset was reduced to 116 candidates, which still constitute a too large pool for a complete calculation of superconducting properties. To reduce the total pool to a manageable number, we hand-picked a few structures (5-6) for each family (D, G, S and T) from the final set of screened candidates. While selecting the structures, care was taken that they represent different values of \( N(E_F) \) and \( \omega_{avg} \) values. For these structures, we performed full calculations of the phonon and \( ep \) coupling spectra over the full BZ. If any of the initially-selected structures was thus found to be dynamically unstable, it was replaced with another candidate with similar values.
of $N(E_F)$ and $\omega_{\text{avg}}$. The positions of the selected structures in the energy vs volume plot in Fig.1 are shown by the dark colored symbols, whereas the rest of the structures are indicated by the light colored symbols.

4. Convex Hull

![Convex hull of the Boron-Carbon system w.r.t. graphite C and amorphous C in top and bottom panel respectively. The reference for B is $\alpha$-R-B_{12}. The reference energy for the amorphous C is obtained from Ref. 39.]

$santanu.saha@tugraz.at$

1. N. W. Ashcroft, Physical Review Letters 21, 1748 (1968).
2. E. Wigner and H. B. Huntington, The Journal of Chemical Physics 3, 764 (1935) [https://doi.org/10.1063/1.1749590].
3. J. A. Flores-Livas, L. Boeri, A. Sanna, G. Profeta, R. Arita, and M. Eremets, Physics Reports (2020), [https://doi.org/10.1016/j.physrep.2020.02.003].
4. M. I. Eremets, A. P. Drozdov, P. P. Kong, and H. Wang, Nature Physics 15, 1246 (2019).
5. P. Loubeyre, F. Occelli, and P. Dumas, Nature 577, 631 (2020).
6. N. W. Ashcroft, Phys. Rev. Lett. 92, 187002 (2004).
7. D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, Scientific reports 4, 6968 (2014).
8. A. Drozdov, M. Eremets, and I. Troyan, arXiv preprint arXiv:1508.06224 (2015).
9. H. Liu, I. I. Naumov, R. Hoffmann, N. Ashcroft, and R. J. Hemley, Proceedings of the National Academy of Sciences 114, 6990 (2017).
10. M. Somayazulu, M. Ahart, A. K. Mishra, Z. M. Geballe, M. Baldini, Y. Meng, V. V. Struzhkin, and R. J. Hemley, Phys. Rev. Lett. 122, 027001 (2019).
11. A. Drozdov, P. Kong, V. Minkov, S. Besedin, M. Kuzovnikov, S. Mozaffari, L. Balicas, F. Balakirev, D. Graf, V. Prakapenka, et al., Nature 569, 528 (2019).
12. L. Boeri and G. B. Bachelet, Journal of Physics: Condensed Matter 31, 234002 (2019).
13. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, nature 410, 63 (2001).
14. J. M. An and W. E. Pickett, Phys. Rev. Lett. 86, 4366 (2001).
15. E. Ekinov, V. Sidorov, E. Bauer, N. Mel’Nik, N. Curro, J. Thompson, and S. Stishov, nature 428, 542 (2004).
16. L. Boeri, J. Kortus, and O. K. Andersen, Phys. Rev. Lett. 93, 237002 (2004).
17. K.-W. Lee and W. E. Pickett, Physical review letters 93, 237003 (2004).
18. X. Blase, C. Adessi, and D. Connétable, Phys. Rev. Lett. 93, 237004 (2004).
19. F. Giustino, J. R. Yates, I. Souza, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. 98, 047005 (2007).
20. H. Rosner, A. Kitaigorodsky, and W. E. Pickett, Phys. Rev. Lett. 88, 127001 (2002).
21. A. N. Kolmogorov and S. Curtarolo, Phys. Rev. B 73, 180501 (2006).
22. G. Savini, A. C. Ferrari, and F. Giustino, Phys. Rev. Lett. 105, 037002 (2010).
23. K. Alberi, M. B. Nardelli, A. Zakutayev, L. Mitas, S. Curtarolo, A. Jain, M. Fornari, N. Marzari, I. Takeuchi, M. L. Green, M. Kanatzidis, M. F. Toney, S. Butenko, B. Meredig, S. Lany, U. Kattner, A. Davydov, E. S. Toberer, V. Stevanovic, A. Walsh, N.-G. Park, A. Aspuru-Guzik, D. P. Tabor, J. Nelson, J. Murphy, A. Sethur, J. Gregoire, H. Li, R. Xiao, A. Ludwig, L. W. Martin, A. M. Rapp, S.-H. Wei, and J. Perkins, Journal of Physics D: Applied Physics 52, 013001 (2018).
24. G. R. Schleder, A. C. M. Padilha, C. M. Acosta, M. Costa, and A. Fazzio, Journal of Physics: Materials 2, 032001 (2019).
25. V. Stanev, C. Oses, A. G. Kusne, E. Rodriguez, J. Paglione, S. Curtarolo, and I. Takeuchi, npj Computational Materials 4, 1 (2018).
26. T. Ishikawa, T. Miyake, and K. Shimizu, Phys. Rev. B 100, 174506 (2019).
27. S. R. Xie, G. R. Stewart, J. J. Hamlin, P. J. Hirschfeld,
and R. G. Hennig, Phys. Rev. B **100**, 174513 (2019).
28 R. J. N. Michael J. Hutchison, Alice M. Shipley, arXiv/cond-mat/2001.09852 (2015).
29 S. Goedecker, The Journal of Chemical Physics **120**, 9911 (2004).
30 S. Goedecker, W. Hellmann, and T. Lenosky, Physical Review Letters **95**, 055501 (2005).
31 M. Amsler and S. Goedecker, The Journal of Chemical Physics **133**, 224104 (2010).
32 A. Jay, O. Hardouin Duparc, J. Sjakste, and N. Vast, Journal of Applied Physics **125**, 185902 (2019).
33 M. Calandra, N. Vast, and F. Mauri, Phys. Rev. B **69**, 224505 (2004).
34 M. Calandra and F. Mauri, Phys. Rev. Lett. **101**, 016401 (2008).
35 J. E. Moussa and M. L. Cohen, Phys. Rev. B **77**, 064518 (2008).
36 J. E. Moussa and M. L. Cohen, Phys. Rev. B **74**, 094520 (2006).
37 J. E. Moussa and M. L. Cohen, Phys. Rev. B **78**, 064502 (2008).
38 W. L. McMillan, Phys. Rev. **167**, 331 (1968).
39 M. Aykol, S. S. Dwaraknath, W. Sun, and K. A. Persson, Science advances **4**, eaao0148 (2018).
40 Y. Lin, Z. Zhao, T. A. Strobel, and R. Cohen, Physical Review B **94**, 245422 (2016).
41 X. Jiang, J. Zhao, Y.-L. Li, and R. Ahuja, Advanced Functional Materials **23**, 5846 (2013).
42 X. Feng, Q. Wu, Y. Cheng, B. Wen, Q. Wang, Y. Kawazoe, and P. Jena, Carbon **127**, 527 (2018).
43 Y. Chen, Y. Xie, S. A. Yang, H. Pan, F. Zhang, M. L. Cohen, and S. Zhang, Nano letters **15**, 6974 (2015).
44 S. Wang, D. Wu, B. Yang, E. Ruckenstein, and H. Chen, Nanoscale **10**, 2748 (2018).
45 Y. Gao, Y. Chen, Y. Xie, P.-Y. Chang, M. L. Cohen, and S. Zhang, Physical Review B **97**, 121108 (2018).
46 Y. Chen, Y. Xie, Y. Gao, P.-Y. Chang, S. Zhang, and D. Vanderbilt, Phys. Rev. Materials **2**, 044205 (2018).
47 R. Baughman and D. Galvao, Chemical physics letters **211**, 110 (1993).
48 J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
49 The threshold of distance for the presence of C-C, B-B and B-C bonds are $d_{CC} \leq 1.5$ Å, $d_{BB} \leq 1.85$ Å and $d_{BC} \leq 1.65$ Å respectively.
50 J. Zhou, Q. Sun, Q. Wang, and P. Jena, Phys. Rev. B **92**, 064505 (2015).
51 S. Mann, P. Rani, R. Kumar, G. S. Dubey, and V. Jindal, RSC advances **6**, 12158 (2016).
52 The vibrational frequencies are calculated for the pure diamond structure with the lattice constant of D05 i.e. a=3.74 Å, which is a ~ 5% larger than the experimental lattice constant of diamond.
53 G. Eliasberg, Sov. Phys. JETP **11**, 696 (1960).
54 J. J. Hopfield, Phys. Rev. **186**, 443 (1969).
55 M. Amsler, “Minima hopping method for predicting complex structures and chemical reaction pathways,” in Handbook of Materials Modeling: Applications: Current and Emerging Materials, edited by W. Andreoni and S. Yip (Springer International Publishing, Cham, 2018) pp. 1–20.
56 M. Amsler, S. Rostami, H. Tahmasbi, E. Rahmatizad, S. Faraji, R. Rasoulkhani, and S. A. Ghasemi, arXiv preprint arXiv:1912.04055 (2019).
57 G. Kresse and F. J., Comput. Mat. Sci. **6**, 15 (1996).
58 G. Kresse and J. Furthmüller, Physical review B **54**, 11169 (1996).
59 G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
60 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
61 S. Grimm, S. Ehrlich, and L. Goerigk, Journal of computational chemistry **32**, 1456 (2011).
62 P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B **49**, 16223 (1994).
63 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scaluzzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, Journal of Physics: Condensed Matter **21**, 395502 (2019).
64 P. Giannozzi, O. Andreussi, T. Brunne, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. D. Jr, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Kücükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. PoncÃc, D. Rocca, R. Sabetani, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, Journal of Physics: Condensed Matter **29**, 465901 (2017).
65 D. Hamann, Physical Review B **88**, 085117 (2013).
66 M. Van Setten, M. Giantomassi, E. Bousquet, M. J. Verstraete, D. R. Hamann, X. Gonze, and G.-M. Rignanese, Computer Physics Communications **226**, 39 (2018).